Energy band alignment at hybrid inorganic-organic semiconductor interfaces, a general many-body perturbation theory approach

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Hybrid inorganic-organic semiconductor interfaces are of interest for new photovoltaic devices operating above the Shockley-Queisser limit. Predicting energy band alignment at such interfaces is crucial for their design, but represents a challenging problem due to the large scales of the system and a wide range of physical phenomena that occur at the interface. In this work, we propose a new method, called the weakly-coupled slabs model, that allows for tractable and accurate computing of the energy band alignment in crystalline hybrid inorganic-organic semiconductor interfaces. As an example, crystalline tetracene physisorbed on the clean hydrogen-passivated 1x2 reconstructed (100) silicon surface has been considered. The proposed method combines the non-self-consistent GW approximation for isolated organic and inorganic slabs, dielectric embedding technique, orbital relaxation corrections for organic semiconductors, and line-up potential method for inorganic semiconductors. For comparison, we have also computed the energy band alignment using the standard GW approach with a supercell model. Comparing the proposed method with the supercell model within the non-self-consistent GW approximation, we have found that the weakly-coupled slabs model reproduces the band offsets more accurately with less computational cost. The maximal deviation from the experimental results is about 120 meV for the band offsets and 50 meV for the tetracene band edges.

I. INTRODUCTION

The interest in crystalline hybrid inorganic-organic semiconductor (HIOS) heterostructures is motivated by their potential to increase the quantum efficiency of photovoltaic devices[8] overcoming the Shockley-Queisser limit[9]. In many modern proposals of HIOS devices, the organic layer facilitates efficient optical generation of excitons via the singlet fission effect, while the inorganic layer provides efficient separation and transport of charge carriers towards the electrode[10]. Such a device operation requires efficient energy and/or charge transfer across the interface[11]. The motivation for this study is recent experimental characterizations of the energy transfer between hydrogen passivated silicon (Si) and tetracene (Tc) that have not shown any significant transfer of the triplet excitons[12]. Also, it has been recently demonstrated experimentally that introducing HfON inorganic inter-layer between Si and Tc can improve the transfer[13]. One of the obstacles preventing efficient energy transfer can be an exciton dissociation at the interface. This process can involve transitions through a series of the inter-layer charge transfer exciton states[14] which, in turn, depend on the energy band alignment. It is therefore crucial to have an accurate understanding of the band alignment in the vicinity of the interface.

A typical band diagram of the HIOS interface is shown in Fig. 1. The widths of energy bands in the organic semiconductor are usually smaller compared to the inorganic part and each band can be associated with a molecular orbital in the isolated molecules constituting the organic semiconductor. The band alignment can be quantitatively characterized by a set of quantities such as the band offsets, $\Delta E_v$ and $\Delta E_c$, ionization potentials, $IP$, work functions, $W$, and electron affinities, $\chi$. The experimental values of these quantities for the Si-Tc heterostructure have been reported in several works[15]. Most of the relevant theoretical works, however, concern only a single molecule physisorbed or chemisorbed at the surface of a metal or inorganic semiconductor[16] or focus on the macroscopic electrostatic effects such as Fermi level pinning and band bending[17]. To the best of our knowledge, there is only one attempt to compute ab-initio the energy bands alignment at the crystalline

FIG. 1. Alignment of the energy bands at the interface between two semiconductors determines the band offsets, $\Delta E_v$ and $\Delta E_c$. The energy band alignment is characterized by the ionization potential ($IP$), electron affinity ($\chi$), band gap ($E_g$) and work function ($W$). For the HIOS, the interface slightly modifies energy bands due to mutual dynamic dielectric screening and interfacial dipole layer ($E_{dip}$).
HIOS interfaces explicitly taking into account electron correlation effects: the recent work (see Ref. 11) reports on the results of energy bands alignment for Tc-Si and pentacene-Si heterostructures obtained using all-electron density functional theory (DFT) with hybrid exchange-correlation functionals. This work computationally predicts the so-called staggered gap heterojunction (II-type) for the Si-Tc interface, while the experimental data shows that this interface must be the straddling gap heterojunction (I-type) according to Refs. 11 and 13. Better progress has been achieved in computing band alignment in inorganic semiconductor heterostructures with a small lattice mismatch. Approximate values for the band offsets can be obtained using Anderson’s rule. Usually, an inaccuracy of Anderson’s rule is associated with the dipole layer that causes an energy shift, $E_d$, of the vacuum level across the interface. For HIOS, additionally to the dipole layer, Anderson’s law can be also violated due to a substantial difference in the nature of electron correlations in the organic and inorganic semiconductors. Unlike electrons in inorganic heterostructures with a small lattice mismatch, electrons in the small vicinity of the HIOS interface have different correlation energies at each side of the interface.

Energies of the band edges are the quantities related to many-body excited states which can be rigorously expressed in terms of quasi-particle wave functions and energies in the framework of the many-body perturbation theory (MBPT). In the case of inorganic semiconductors, however, the band edges can be obtained from DFT computations using the method proposed by Van-de-Walle and Martin. According to this method, DFT is used to compute the positional dependence of the microscopic energy landscape of the hetero-interface taking into account the band bending and dipole layer at the interface. Equipped with the computed electrostatic potential, one can align the band edges computed or measured for bulk semiconductors relatively to this potential and get the correct band offsets assuming that the difference in the exchange-correlation effects at each side of the heterojunction is negligibly small.

The goal of this work is to estimate the role of the correlation effects at the crystalline HIOS interface represented by the Tc/Si heterostructure and to develop a computational method that can accurately estimate the energy band alignment at such interfaces. In Sec. II, we determine the atomic structure of the Tc/Si interface, report the results of DFT computations for the energy band alignment and show that the mean-field theory can lead to a spurious charge transfer across the interface. In Sec. III, we present the results of the energy band alignment computations using MBPT with the $\Gamma_0$ approximation and discuss two approaches: standard GW computations for a supercell and our new approach based on the dielectric embedding method for weakly-coupled slabs. Originally, the dielectric embedding technique has been developed to reduce computational cost for the system consisting of a single molecule physisorbed on extended surfaces. We extend this approach for crystalline weakly-coupled HIOS interfaces and use it to prevent spurious charge transfer in the $\Gamma_0$ approximation. In this section, we also discuss the corrections aimed to compensate the errors that originate from neglecting orbital relaxation and from finite sizes of the Si slab. In Sec. IV, we summarize our results and discuss the general applicability of our method.

II. ATOMIC STRUCTURE OF THE TC/SI INTERFACE, DFT RESULTS

Experimentally it has been observed that Tc can be deposited onto neutral surfaces either in so-called “flat-lying” or “upright-standing” configuration. In the first case, the angle between the long molecular axis and surface is small, while in the second case this angle is close to 90°. In this work we are interested in the latter case, since it is characterized by a denser coverage of organic molecules and, therefore, one may expect higher mobility of charge carriers in Tc that is a desirable property for electronic applications.

We focus on one particular Tc/Si heterostructure with a relatively small crystal lattice mismatch that has been also thoroughly characterized experimentally, the contact between the “upright-standing”-configuration sur-
face of the crystalline Tc and hydrogen-passivated 1x2 reconstructed (100) Si surface, shown in Fig. 2.

All computations in this work are performed for a slab model containing 16 atomic layers of Si and two molecular layers of Tc. We need at least two molecular layers to simulate accurately the electronic environment for the Tc molecules at the interface. A single layer would be the surface layer\(^{22}\).

The atomic coordinates have been obtained from the geometry optimization within DFT with a plane-wave basis set and norm-conservative pseudo-potentials\(^{23,24}\). The computations were performed using Quantum Espresso, the plane-wave DFT software\(^{25,26}\). The dispersion forces, responsible for the physisorption of Tc on the Si surface, are introduced in the model via the non-local exchange-correlation functional \(\text{vdW-DF2-C09}^{27}\). The computations have been performed on the 4x3x1 Monkhorst-Pack \(k\)-space grid, using a kinetic energy cut-off of 80 Ry for wavefunctions and 320 Ry for charge densities. These choices are justified by a series of convergence tests (see Supplementary info). For the geometry optimization, we used the use Broyden-Fletcher-Goldfarb-Shanno quasi-newton algorithm with variable cell parameters. The system is periodic only in two in-plane dimensions. The effect of the periodic boundary conditions in the third dimension was canceled by the dipole correction\(^{28}\).

The 1x2 reconstructed Si(100) surface has a rectangular unit cell with lateral sizes of \(\sqrt{2}a_{\text{Si}}\) and \((\sqrt{2}/2)a_{\text{Si}}\) along the axes [110] and [110] respectively, where \(a_{\text{Si}}\) is the lattice constant of bulk Si. The minimal unit cell spans giving the best match of sublattices are \(1 \times 2\) for Tc and \(1 \times 3\) for Si, shown schematically in Fig. 2. In order to estimate the mismatch, we take the lattice constants reported in the literature \(a_{\text{Si}} = 5.4\) Å for Si and \(a_{\text{Tc}} = 7.9\) Å and \(b_{\text{Tc}} = 6.03\) Å for Tc, then \(\sqrt{2}a_{\text{Si}} = 7.64\) Å and \(3 \times (\sqrt{2}/2)a_{\text{Si}} = 11.462\) Å that makes the mismatches along each of the axes being 0.26 Å and 0.6 Å.

The computed lateral sizes of the unit cell are 7.74 Å and 11.61 Å. These values are close to the experimentally observed lattice constants published in Ref. 21 for the crystalline Tc deposed on the 1x2 reconstructed (100) Si surface: \(a_{\text{Tc}} = 7.3 \pm 0.6\) Å and \(2b_{\text{Tc}} = 2 \times 5.5 \pm 0.6 = 11.0 \pm 0.6\) Å. Comparing to the results for isolated slabs, we find that the Si slab remains almost undeformed imposing slight deformations on the Tc lattice. This can be explained by the fact that, comparing to deformations in Si, deformations of Tc require less energy due to the van-der-Waals nature of bonding in the molecular crystal.

The results of the geometry optimization also show that the most dramatic changes occur in the surface Tc layer, which agrees with the results of Ref. 22.

Using DFT with the parameters described above, we have computed the electrostatic potential and charge density in the Si/Tc super-cell. To estimate the mutual effect that Si and Tc layers make on each other, it is useful to compare the results for the heterostructure with the results for free surfaces given the atomic configuration remains unchanged. Qualitatively, this mutual effect can be expressed by the change in the electrostatic potential and charge density (see Fig. 3):

\[
\Delta V^H = V^H_{\text{Si/Tc}} - V^H_{\text{Si}} - V^H_{\text{Tc}},
\]

\[
\Delta \rho = \rho_{\text{Si/Tc}} - \rho_{\text{Si}} - \rho_{\text{Tc}},
\]

where the index \(\text{Si/Tc}\) corresponds to the computations in the super-cell, and the indices \(\text{Si}\) and \(\text{Tc}\) correspond to the quantities computed for the isolated Si and Tc slabs respectively.

The step-wise electrostatic potential and corresponding charge density change, shown in Fig. 3, are characteristic of the interfacial dipole layer. The formation of the dipole layer between the neutral Si surface and crystalline Tc has not been confirmed experimentally\(^3\) and is attributed to a spurious charge transfer. The reason why such a charge transfer occurs can be understood by taking a look at the band structure for isolated Si and Tc slabs (see Fig. 4). The DFT results show that the maximum of the valence band in Tc is located higher than the minimum of the conduction band in Si making possible the electron tunnelling from the occupied states in Tc to the unoccupied states in Si. Such an energy band alignment defines the II-type heterostructure.

For the Tc band structure, projections of the Kohn-Sham orbitals on the rectangular box confining a single molecular layer have been computed (blue and red markers in Fig. 4). Due to weak van-der-Waals coupling between molecular layers, the projections take two values making it possible to classify energy bands according to their location in the first (closer to Si) or second molecular layer (surface layer). As a result, we can estimate band edges for each molecular layer. In the surface layer, according to our DFT computations, the band-gap is slightly larger and the valence and conduction band edges are shifted by about 50 and 100 meV respectively towards the vacuum level.

The DFT results for the Si/Tc super-cell are not the best choice for the basis set for further GW calculations since they may suffer from a spurious charge transfer and contain a contribution from a false dipole layer. In principle, the error associated with this charge transfer can be eventually eliminated in the process of the self-consistent GW computations. But the idea is to perform GW in a non-self-consistent way (single shot) to avoid the large computational cost of repeated self-consistent loops. This leads us to the idea that, if we want to achieve a satisfactory accuracy within the non-self-consistent \(\text{G}_0\text{W}_0\) approximation, the better choice of the basis set for MBPT would be Kohn-Sham orbitals of the isolated slabs.
FIG. 3. Change of a) the Hartree potential and b) electron density in the Tc/Si slab relative to isolated Si and Tc slabs with the same atomic configuration.

III. MANY-BODY PERTURBATION THEORY RESULTS

A. $G_0W_0$ approximation

DFT usually significantly underestimates band-gaps and ionization potentials. This discrepancy is related to an error produced by an approximated exchange-correlation functional, which is in turn associated with a so-called delocalization error, known also as many-electron self-interaction error. Better accuracy in modeling exchange-correlation effects can be achieved using MBPT in the GW approximation. Energy corrections to the orbital energies within MBPT in the GW approximation are given by expectation values of the quasi-particle self-energy defined by Hedin’s equations:

$$\varepsilon_i = \langle \phi_i | \Sigma [GW] | \phi_i \rangle$$  \hspace{1cm} (3)

$$W = \varepsilon^{-1}v = [1 - v\chi]^{-1}v$$  \hspace{1cm} (4)

where: $\phi_i$ is an element of the basis set (usually Kohn-Sham orbitals), $\Sigma [GW]$ is the self-energy matrix dependent on the retarded Green’s function, $G$, and screened Coulomb potential, $W$, $\varepsilon^{-1}$ is the dielectric matrix inverse, $v$ is the bare Coulomb potential, and $\chi$ is the irreducible polarizability.

Since the system under consideration is rather large (348 atoms in the super-cell), it is desirable to avoid an iterative approach and use the non-iterative $G_0W_0$ approximation. The standard routine for this method implies the following sequence of computations: 1) compute the basis set represented by Kohn-Sham orbitals using DFT; 2) compute the irreducible polarizability, dielectric matrix and its inverse in the random phase approximation (Eq. (4)) using the basis set computed at the previous step; 3) compute the self-energy corrections to the DFT eigen-energies (Eq. (3)) applying the first-principles methodology of Hybertsen and Louie with the generalized plasmon-pole model for the frequency-dependent dielectric matrix.

For the first step, we use the results obtained in Sec. II, keeping all the parameters unchanged. For the second and third steps, all the computations related to MBPT have been performed using BerkeleyGW. In ab-initio MBPT computations, it is important to ensure convergence of the results by properly choosing the kinetic energy cutoff for the dielectric matrix and the number of unoccupied bands participating in sums both in the dielectric matrix and Coulomb-hole self-energy. In the latter case, the convergence is rather slow (see the convergence tests in the Supplementary information). In this work we use two techniques to reduce the number of the bands explicitly participating in the computations: first, we apply the modified static remainder approach and use the extrapolation technique based on fitting the Coulomb-hole self-energy by a hyperbolic function. After a series of convergence tests discussed in Supplementary information we have derived the following parameters: the kinetic energy cutoff for the dielectric matrix is of 15 Ry, the sums run over 534 unoccupied orbitals (1200 orbitals in total), and the k-grid is same as for the DFT calculations discussed in Sec. II.

In Fig. 5 we show results of band edge computations for the supercell model, defined in Sec. II, using different computational approaches. Expectedly, the band structures obtained with MBPT have larger band gaps for both Tc and Si in comparison to those obtained by DFT (compare diagrams A and B in Fig. 5). What is more...
surprising is that the shifts of the band edges in Si and Tc are qualitatively different. For Tc, the GW corrections to the valence and conduction band edges are more less the same, whereas for Si, the corrections substantially decrease the energy of the valence band edge while the conduction band edge remains almost unchanged. According to the results of Ref. 36, such behaviour for GW corrections for Si is the case for most of the inorganic III-V and IV semiconductors. Since the energy difference between DFT and GW results is determined by the electron correlation effects, we conclude that the nature of electron correlations is substantially different in Tc and Si slabs.

Comparing the results obtained by the G$_0$W$_0$ method (diagram B, Fig. 5) to experimental data, we find significant discrepancy: the energy of the valence band edge is largely underestimated for Si (about 0.6 eV) and the valence band edge for Tc is about 200 meV larger than the experimental value. In the case of Tc this discrepancy can be explained by the fact that we use the G$_0$W$_0$ approximation neglecting orbital relaxation. In the case of Si, due to largely delocalized wave functions, the source of the error is the slab model which is prone to the quantum confinement effect and is characterized by a modified electrostatic environment that reduces the dielectric screening for the G$_0$W$_0$ method.

B. Orbital relaxation corrections and line-up potential method

1. Tc slab

The discrepancy between the G$_0$W$_0$ and GW approximations is attributed to the orbital relaxation observed as a change of orbital energies due to rearrangement of electrons in the fields of nuclei when we add or remove an electron in/from the system. For the case of organic semiconductors with small orbit hybridization between molecules, we propose an ansatz, according to which the orbital relaxation after removal of an electron from an isolated molecule gives approximately the same energy correction as it would be in the van-der-Waals molecular crystals. This approach is similar to the so-called QM/QM’ method and leads to the following expressions for the band edges in molecular crystals:

\[
\varepsilon_j = \varepsilon_{j}^{G_0W_0/crys} - (\varepsilon_{j}^{G_0W_0/mol} - \Delta E_j^{mol})
\]

\[
\Delta E_i^{mol} = E_i^{mol}(N \pm 1) - E^{mol}(N)
\]

The energy difference in the parentheses in Eq. (5) is shown in Fig. 6 where we compare different computational approaches used to compute HOMO and LUMO energies for a single Tc molecule. The difference between the results obtained by the LDA and ∆SCF methods is the origin of so-called Koopmans’ corrections in DFT. This discrepancy is attributed to the so-called delocalization error or many-electron self-interaction error manifesting itself as an incorrect dependence of the total energy on the fractional number of electrons (convex instead of linear). The error is caused by neglecting the electron correlation effects and orbital relaxation. The G$_0$W$_0$ approach, in turn, takes into account the correlation effects neglecting the orbital relaxation. Therefore, the difference between the ∆SCF and G$_0$W$_0$ energies can be attributed to the orbital relaxation effect only. These corrections for HOMO and LUMO are very close to each other and decrease the orbital energies as is expected after the orbital relaxation. Note that the atomic configuration of the Tc molecule for computing the energy corrections is taken unchanged from the Tc slab after the geometry optimization in the supercell.

This method is consistent with the recently proposed Wannier-Koopmans method. The relationship between two approaches in the approximation of negligible orbital hybridization between organic molecules is discussed in Appendix A.
The valence band edge in Si obtained by the G₀W₀ approach (diagram B in Fig. 5) is about 0.6 eV lower in comparison to the experimental data, while the position of the conduction band edge is accurate within 50 meV. Similar results are reported in Ref. [36] where the ionization energy for the Si slab with the (111) 2x1 reconstructed surface is -5.64 eV which is pretty close to our results: -5.71 eV for the free surface and -5.618 eV for the surface in contact with the Tc bi-layer. The different types of surface termination (the (111)-surface against the (100)-surface) does not lead to the difference of more than 0.1 eV and its effect is not important for this consideration. In all these cases, some of the discrepancies between the experimental data and the results of the computations can be attributed to the fact that the experimental data are reported for surfaces of the bulk semiconductors while the computations are performed for the slab models where the band edges are shifted due to the quantum confinement and truncated dielectric screening in slabs. In order to accurately simulate a bulk semiconductor, the slab thickness has to be about 5 nm which, together with the Tc slab, makes the system extremely large and practically intractable for most of the computational methods of quantum chemistry.

This discrepancy, however, can be somewhat compensated using the line-up potential method [39,40]. This method relies on the idea that local physical quantities, such as the electrostatic potential, in the middle of the slab should coincide with the analogous quantities for the bulk configuration. The DFT computations for the bulk materials give the valance and conduction band edges measured relative to the averaged electrostatic potential (see Fig. 7). These quantities are not prone to the quantum confinement effect and reduced screening in the slab model. However, the computations for the slab model are still needed to estimate the vacuum level relative to the electrostatic potential and, correspondingly, the band edges in order to obtain the ionization potential and electron affinity: the band edges ordained from the bulk case can be properly aligned relative to the vacuum level of the slab by equating the averaged electrostatic potentials in the bulk and slab (see Fig. 7).

3. Effect of the corrections

Adding the orbital relaxation corrections computed with Eq. (5) and (6) and computing Si band edges using the line-up potential method improve agreement of the results with experimental data (see diagram C in Fig. 5). This combination of the G₀W₀ approach, orbital relaxation correction and line-up potential method predicts an I-type heterostructure for the Si/Tc interface, as is experimentally observed. The resulting corrections for Tc and Si are so different that they are capable of switching the II-type heterostructure (predicted by DFT) to the I-type (predicted by MBPT/GW). In inorganic heterostructures, the GW corrections are approximately the same for all semiconductors, so the band offsets predicted by DFT remain unchanged after GW corrections. Therefore, the case when the electron correlations determine the band offsets is specific for HIOS interfaces only and shows the extraordinary importance of the correlation effects for them.

The computed band offsets are 0.23 meV for the valence band and 1.247 eV for the conduction band. The absolute errors for the bands offsets are 30 meV for the valence band and 452 meV for the conduction band.

C. Weakly-coupled slabs model

The supercell model still contains inaccuracy associated with the spurious charge transfer and dipole layer
FIG. 8. Band edge alignment at the Si/Tc interface for the weakly-coupled slabs model. The diagram D corresponds to the DFT data for the isolated slabs; the diagram E is for the data obtained for the isolated slabs in the G0W0 approximation; the diagram F represents the results computed with the dielectric embedding (DE) method and G0W0 approximation; the diagram G contains the data computed using a combination of the G0W0 approach, line-up potential model for Si, DE and orbital relaxation correction for Tc. The experimental results (the right-most diagram) are taken from Ref. [1].

Discussed briefly in Sec. II. Since the non-self-consistent flavor of the GW method is used, the spurious charge transfer affects the MBPT results as well: the band gap in the first Tc molecular layer is 277 meV smaller than in the second layer. Such a large variation of the band gaps in Tc layers cannot be solely attributed to different electrostatic environments and dielectric screening for two layers and is resulted from the effect of the dipole layer. Another manifestation of the dipole layer effect is increasing of the band offset in the valence band and reduction of the band offset in the conduction band (comparing to experimental data).

In this work, to solve the problem of the spurious charge transfer, we propose a new model for weakly-coupled slabs. The weakly-coupled slabs model utilizes the basis set consisting of the Kohn-Sham orbitals of isolated Tc and Si slabs. The band edges corresponding to these Kohn-Sham orbitals are shown in Fig. 8 (diagram D). If we proceed with the isolated slabs and compute GW corrections (diagram E in Fig. 8), we find that the band gaps in both Tc and Si are dramatically overestimated compared to the supercell model (diagram B in Fig. 5). This is due to neglecting the mutual dynamic dielectric screening and induced polarization that occur when two slabs are in contact.

In order to take into account mutual dielectric screening of the slabs, we use the dielectric embedding technique for the GW method. This technique is based on the idea that, if slabs are weakly coupled and the orbital hybridization between them can be neglected, the basis set \( \phi_i \) in Eqs. (3) and (4) can be split into two subsets of non-overlap functions for the Tc and Si slabs, \( \phi_i^{Tc} \) and \( \phi_i^{Si} \), and the Green’s function in this representation reads \( G = G^{Si} + G^{Tc} \). As a result, the GW energy corrections can be computed independently for Si and Tc slabs:

\[
\Sigma \approx \Sigma^{Si} + \Sigma^{Tc} = \langle \phi_i^{Si}|G^{Si}W|\phi_i^{Si} \rangle + \langle \phi_i^{Tc}|G^{Tc}W|\phi_i^{Tc} \rangle. \tag{7}
\]

The slabs are coupled only via the screened potential \( W \) with the mutual electrostatic effects and long-range electron-electron correlation quantitatively expressed by the frequency-dependent dielectric function \( \epsilon^{-1} = [1 - v\chi]^{-1} \) in Eq. (4). The dielectric embedding is based on the assumption that the polarizability matrix \( \chi \) is additive and can be computed independently for each slab:

\[
\chi \approx \chi^{Si} + \chi^{Tc}. \tag{8}
\]

The bottleneck in the numerical computations is computing the matrix inverse.

Originally, the idea of the dielectric embedding in MBPT has been proposed to speed up the GW computations reducing sizes of the super-cell when computing \( G \), \( \chi \) and \( \Sigma \) for organic molecules weakly coupled to metallic substrates. In this work, we use this method for another reason: to prevent the spurious charge transfer in DFT computations discussed in the previous section taking into account mutual dynamic electrostatic screening between Tc and Si slabs. The dielectric embedding leads to neglecting all the propagators that involve particle propagation between organic and inorganic semiconductors, keeping only diagrams where two semiconductors are coupled by exchanging virtual photons (see Fig. 9). This follows from Eq. (7) where the self-energy is expressed in terms of Green’s functions for which both initial and final states belong either to Tc or to Si. In the dielectric embedding, the coupling between slabs is included into consideration only via the screened Coulomb...
Si Tc

\[ P_{e} = E_{0}^{GW0/DE} - E_{0}^{GW0/split} \]
\[ P_{n} = E_{0}^{GW0/DE} - E_{c}^{GW0/split} \]

This reduces errors associated with the basis set used in MBPT that is prone to a spurious charge transfer and allows us to obtain accurate results within the non-self-consistent G\(_{0}\)W\(_{0}\) approximation.

The comparison between the GW results for isolated slabs (diagram E in Fig. 8) and the result computed with the dielectric embedding (diagram F in Fig. 8) allows us to estimate the polarization that Si induces in Tc when two materials are in contact. This polarization can be quantitatively characterized by two quantities: \( P_{p} = E_{0}^{GW0/DE} - E_{0}^{GW0/split} \) and \( P_{n} = E_{0}^{GW0/DE} - E_{c}^{GW0/split} \). Since these quantities are defined by long-range dielectric screening effects, they are not sensitive to small local variations of electron density in the slabs and, therefore, should be more or less independent of the choice of the DFT parameters, such as exchange-correlation functionals and pseudopotentials. Consequently, the polarization \( P_{p} \) and \( P_{n} \), computed within G\(_{0}\)W\(_{0}\) approximation with dielectric embedding, should be transferable and can be used as energy corrections that take into account the effect caused by slab coupling with any computational method applied to the isolated slabs.

The dielectric embedding leads to smaller band gaps in both materials, however these changes are more pronounced for the organic semiconductor and for the first molecular layer. This effect is similar to the results of previous studies of the dependence of the frontier orbitals of a single organic molecule on the distance to a metallic substrate. 

After computing the GW corrections with the dielectric embedding, we apply the orbital relaxation corrections for the organic semiconductor and the line-up potential method for the inorganic semiconductor as we did for the supercell model. The resulting band edges, shown in diagram G in Fig. 8, are in good agreement with the experimental data. We find that the difference of the band gaps in two molecular layers is 128 meV that is 99 meV smaller compared to the supercell model. The computed band offsets are 0.089 meV for the valence band and 1.815 eV for the conduction band. The corresponding absolute errors for the bands offsets are 111 meV and 115 meV. Compared to the supercell model, the error is distributed more evenly between the valence and conduction bands. The main contribution to this discrepancy comes from the Si part. The bandgap for Si, computed using the G\(_{0}\)W\(_{0}\) method, is 1.118 eV being in good agreement with the experimental value of 1.12 eV. However, the ionization potential and electron affinity, given by the line-up potential method, are both about 100 meV lower relative to the experimentally observed values for the free Si surface. The proposed method has shown the best performance in predicting the band edges in the crystalline Tc - the absolute error does not exceed 50 meV.

**IV. DISCUSSION AND SUMMARY**

The results of this work have demonstrated the exceptional importance of electron correlation and screening effects in modelling the energy band alignment at HIOS interfaces. Unlike for the inorganic heterostructures, the mean-field theories for HIOS are not able to predict the energy band alignment even qualitatively. On the other hand, both MBPT approaches, the supercell model and the weakly-coupled slabs model, predict qualitatively correct energy band alignment of the Si/Tc interface that is of the I-type. The latter model, however, gives better agreement for the Tc bandgap in the first molecular layer as well as smaller aggregated error for the conduction and valence bands offsets. For Tc, the weakly-coupled model shows agreement with the experimental data within 50 meV.

The procedure discussed in the previous sections can be used for any HIOS interface in general if physisorption significantly exceeds chemisorption. The summary of the proposed weakly-coupled slabs model is shown in Fig. 10 in the form of a block-diagram. The first step is the geometry relaxation within DFT. Keeping all atomic coordinates fixed, we split the supercell into Si and Tc parts to prevent spurious charge transfer that can occur in DFT. Then, we compute the basis set functions and Hartree potentials for isolated slabs using DFT. To take into account a mutual dielectric screening of the slabs, we apply the dielectric embedding technique: first, we compute the polarizabilities for the isolated slabs, then we sum them up, compute dielectric matrix and invert it. The resulting dielectric matrix is used to compute quasiparticle energies in Tc. These energies are then corrected with the orbital relaxation corrections. In parallel, we compute the band edges in Si using the line-up potential method, GW method to get band edges in bulk Si, and Hartree potential for the Si slab to line them up. At the final step, if the energy bands overlap or in the case of the structure with doping and room temperature, we need to take into consideration possible charge transfer and formation of dipole layers. This can be done if we further apply a simplified procedure published in Refs. 22,24. This approach is based on the 1D semi-classical electrostatic model and has shown good agreement with experimental data for a range of organic heterostructures. Since in this

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**FIG. 9.** Examples of Feynman diagrams representing the terms in the Green’s function expansion involving a) exchanging of virtual photon and b) exchanging electrons between slabs. In the weakly-coupled slabs model the diagrams of the second kind are neglected.
Work we study undoped semiconductors at 0 K without the overlap of energy bands, the last step is not required.

The computational cost associated with the weakly-coupled slabs model can be significantly reduced compared with the conventional supercell model if the former uses smaller unit cells for isolated slabs. In order to sum the polarizability matrices in Eq. [8] the unit cells of different sizes have to be brought to the same sizes in the reciprocal space by zero padding in the real space and further Fourier transform. Also, computing the self-energies for isolated slabs within the dielectric embedding method converge faster with respect to the number of occupied bands as compared to the supercell model. Using less unoccupied bands in the expansions also reduces the computational cost. Moreover, computations for different organic compounds on the same substrate do not require repeated computing of the dielectric matrix for the inorganic part.

The proposed method can be applied to a wide range of crystalline HIOS interfaces with negligible orbital hybridization. The weakly-coupled-slabs model is not prone to spurious charge transfer and leads to qualitative accuracy in the framework of the non-self-consistent G0W0 approximation. A series of computational experiments in this work show that a combination of the dielectric embedding method and the line-up potential method is capable to reproduce accurately the electron correlation and screening effects in HIOS systems without repeatable self-consistent computations.

V. ACKNOWLEDGEMENTS

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Appendix: A

In the Wannier-Koopmans method, the correction for the orbital energies reads:

$$\varepsilon_j = \varepsilon_j^{\text{LDA}} + \sum_i \lambda_i s_{ij}$$  \hspace{1cm} (A.1)

where: $\varepsilon_j^{\text{LDA}}$ is the energy of $j$th Kohn-Sham orbital computed using LDA-DFT; $s_{ij} = |\langle \phi_i | \psi_j \rangle|^2$ is the squared overlap integral between a Wannier function $\phi_i$ and the Kohn-Sham orbital $\psi_j$, and $\lambda_i$ is the energy correction defined by:

$$\lambda_i = \frac{\partial \tilde{E}_i(s_i)}{\partial s_i} \bigg|_{s_i=0}$$  \hspace{1cm} (A.2)

where:

$$\tilde{E}_i(s_i) = [E_i(N \pm 1) - E(N)] \times s_i - [E_i(N \pm s_i) - E(N)]$$  \hspace{1cm} (A.3)

The corrections in Eq. (A.1) are formally similar to the corrections in the Hubbard corrected DFT+U functionals and, in both cases, they are related to the electron correlation effects. In what follows, we consider the case of the organic crystals consisting of $n$ identical weakly coupled molecules per unit cell with negligible orbital hybridization between them. Since all molecules are identical and assuming that the crystal field does not cause the orbital mixing effect (no hybridization) and $\sum_i s_{ij} = 1$, the correction $\lambda_i$ is identical for each term of the sum and Eq. (A.2) can be simplified:

$$\varepsilon_j = \varepsilon_j^{\text{LDA}} + \lambda_j$$  \hspace{1cm} (A.4)
Computing the derivative in Eq. (A.1) explicitly leads to the following expression for $\lambda_j$:

$$\lambda_i = \Delta E_i - \frac{\partial E_i(N \pm s_i)}{\partial s_i} \bigg|_{s_i=0}$$  \hspace{1cm} (A.5)

where $\Delta E_i = E_i(N \pm 1) - E(N)$ is the charging energy of a molecule in the crystalline environment. The second term in the right-hand-side part is the Kohn-Sham energy according to the Janak's theorem and, therefore, $\lambda_i = \Delta E_i - \varepsilon_{i}^{LDA}$ that leads us to:

$$\varepsilon_j = E_i(N \pm 1) - E(N)$$  \hspace{1cm} (A.6)

The problem is now reduced to computing the charging energies $E_i(N \pm 1)$ of a molecule in a crystalline environment. One way of doing this would be using some effective medium model such as the polarizable continuum model. However, in this work we try to consistently stay within the MBPT/G0W0 approach. For this reason, we rewrite Eq. (A.6) expressing explicitly energies of the isolated molecule, $E_i^{mol}(N)$:

$$\varepsilon_j = E_i^{mol}(N \pm 1) - E^{mol}(N) + \Delta_j$$  \hspace{1cm} (A.7)

where $\Delta_j$ is the polarization energy related to the effect that crystal fields cause on the orbital energies for a molecule in a crystalline environment. We express the polarization energy in the framework of the G0W0 approximation:

$$\Delta_j = \varepsilon_j^{G0W0/crys} - \varepsilon_j^{G0W0/mol}.$$  

This difference gives the non-local correction to the orbital energies taking into account the effect of the crystalline environment on the quasi-particle energies. Adding these corrections to the orbital energies $\Delta E_i^{mol}$, obtained by the SCF for the isolated molecule, restores Eq. (5).

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1. R. W. MacQueen, M. Liebhaber, J. Niederhausen, M. Mews, C. Gersmann, S. Jäckle, K. Jäger, M. J. Y. Tayebjee, T. W. Schmidt, B. Rech, and K. Lips, Mater. Horiz. 5, 1065 (2018).
2. W. Shockley and H. J. Queisser, Journal of Applied Physics 32, 510 (1961).
3. M. Einzinger, T. Wu, J. F. Kompalla, H. L. Smith, C. F. Perkinson, L. Nienhaus, S. Wiegold, D. N. Congreve, A. Kahn, M. G. Bawendi, and M. A. Baldo, Nature 571, 90 (2019).
4. J. Niederhausen, R. W. MacQueen, E. Özkol, C. Gersmann, M. H. Futschler, M. Liebhaber, D. Friedrich, M. Borgwardt, K. A. Mazzio, P. Amsalem, M. H. Nguyen, B. Daiber, M. Mews, J. Rappich, F. Ruske, R. Eichberger, B. Ehrler, and K. Lips, The Journal of Physical Chemistry C 124, 27867 (2020).
5. R. Schlesinger, Energy-Level Control at Hybrid Inorganic/Organic Semiconductor Interfaces (Springer International Publishing, 2016).
6. Y. Zhou, Optoelectronic Organic-Inorganic Semiconductor Heterojunctions (CRC Press, 2021).
7. A. A. Bakulin, S. D. Dimitrov, A. Rao, P. C. Y. Chow, C. B. Nielsen, B. C. Schroeder, I. McCulloch, H. J. Bakker, J. R. Durrant, and R. H. Friend, The Journal of Physical Chemistry Letters 4, 209 (2013).
8. Z.-F. Liu, D. A. Egger, S. Refaely-Abramson, L. Kronik, and J. B. Neaton, The Journal of Chemical Physics 146, 092326 (2017).
9. J. B. Neaton, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. 97, 216405 (2006).
10. I. Tamblyn, P. Darancet, S. Y. Quek, S. A. Boney, and J. B. Neaton, Phys. Rev. B 84, 201402 (2011).
11. S. M. Janke, M. Rossi, S. V. Levchenko, S. Kokott, M. Scheffler, and V. Blum, Electronic Structure 2, 035002 (2020).
12. T. Ihn, Semiconductor Nanostructures: Quantum States and Electronic Transport (OUP Oxford, 2010).
13. According to Anderson's rule, the conduction band offset is equal to the difference of electron affinities and the valence band offset is given by the difference of the ionization energy for the semiconductors constituting the heterostructure. This law implies that the vacuum level is constant and doesn't change across the hetero-junction.
14. J. H. Davies, The Physics of Low-dimensional Semiconductors: An Introduction (Cambridge University Press, 1997).
15. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 801 (2002).
16. D. Golze, M. Dvorak, and P. Rinke, Frontiers in Chemistry 7, 377 (2019).
17. C. G. Van de Walle and R. M. Martin, Phys. Rev. B 35, 8154 (1987).
18. Z.-F. Liu, F. H. da Jornada, S. G. Louie, and J. B. Neaton, Journal of Chemical Theory and Computation 15, 4218 (2019).
19. M. G. Betti, A. Kanjilal, and C. Mariani, The Journal of Physical Chemistry A 111, 12454 (2007).
20. B. Jaeckel, T. Lim, A. Klein, W. Jagermann, and B. A. Parkinson, Langmuir 23, 4856 (2007).
21. A. Tersigni, J. Shi, D. T. Jiang, and X. R. Qin, Phys. Rev. B 74, 205326 (2006).
22. H. Morisaki, T. Koretsune, C. Hotta, J. Takeya, T. Kimura, and Y. Wakabayashi, Nature Communications 5, 5400 (2014).
23. D. R. Hamann, Phys. Rev. B 88, 085117 (2013).
24. M. van Setten, M. Giantomassi, E. Bousquet, M. Verstraete, D. Hamann, X. Gonge, and G.-M. Rignanese, Computer Physics Communications 226, 39 (2018).
25. G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 801 (2002).
and S. Baroni. *Journal of Physics: Condensed Matter* **29**, 465901 (2017).

20. P. Giannozzi, O. Baseggio, P. Bonfà, D. Brunato, R. Car, I. Carnimeo, C. Cavazzoni, S. de Gironcoli, P. Delugas, F. Ferrari Ruffino, A. Ferretti, N. Marzari, I. Timrov, A. Urru, and S. Baroni, *The Journal of Chemical Physics* **152**, 154105 (2020). [https://doi.org/10.1063/5.0005082](https://doi.org/10.1063/5.0005082).

21. V. R. Cooper, *Phys. Rev. B* **81**, 161104 (2010).

22. L. Bengtsson, *Phys. Rev. B* **59**, 12301 (1999).

23. S. McKechnie, G. H. Booth, A. J. Cohen, and J. M. Cole, *The Journal of Chemical Physics* **142**, 194114 (2015). [https://doi.org/10.1063/1.4921037](https://doi.org/10.1063/1.4921037).

24. A. J. Cohen, P. Mori-Sánchez, and W. Yang, *Science* **321**, 792 (2008), [https://www.science.org/doi/pdf/10.1126/science.1158722](https://www.science.org/doi/pdf/10.1126/science.1158722).

25. L. Hedin and S. Lundqvist (Academic Press, 1970) pp. 1–181.

26. M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).

27. J. Deslippe, G. Samsonidze, D. A. Strubbe, M. Jain, M. L. Cohen, and S. G. Louie, *Computer Physics Communications* **183**, 1269 (2012).

28. J. Deslippe, G. Samsonidze, M. Jain, M. L. Cohen, and S. G. Louie, *Phys. Rev. B* **87**, 165124 (2013).

29. I. Tamblyn, P. Darancet, S. Y. Quek, S. A. Bonev, and J. B. Neaton, *Phys. Rev. B* **84**, 201402 (2011).

30. W. Chen and A. Pasquarello, *Phys. Rev. B* **90**, 165133 (2014).

31. J. Ma and L.-W. Wang, *Scientific Reports* **6**, 24924 (2016).

32. J. Ma, Z.-F. Liu, J. B. Neaton, and L.-W. Wang, *Applied Physics Letters* **108**, 262104 (2016).

33. I. Borriello, G. Cantele, D. Ninno, G. Iadonisi, M. Cossi, and V. Barone, *Phys. Rev. B* **76**, 035430 (2007).

34. I. Marri, M. Amato, M. Bertocchi, A. Ferretti, D. Varsano, and S. Ossicini, *Phys. Chem. Chem. Phys.* **22**, 25503 (2020).

35. Z.-F. Liu, *The Journal of Chemical Physics* **152**, 054103 (2020). [https://doi.org/10.1063/1.5140972](https://doi.org/10.1063/1.5140972).

36. M. Oehzelt, N. Koch, and G. Heimel, *Nature Communications* **5**, 4174 (2014).

37. M. Oehzelt, K. Akaike, N. Koch, and G. Heimel, *Science Advances* **1**, e1501127 (2015).

38. H. Sun, S. Ryno, C. Zhang, M. K. Ravva, Z. Sun, T. Körzölröfer, and J.-L. Brédas, *Journal of Chemical Theory and Computation* **12**, 2906 (2016).

39. M. V. Klymenko, J. A. Vaitkus, and J. H. Cole, *ACS Applied Electronic Materials* **1**, 1667 (2019).
Supplementary Materials

In the supplementary materials we provide information justifying the choice of the computation parameters for DFT and MBPT methods.

1. DFT parameters

In this work, the computations based on DFT rely on the norm-conserved pseudopotentials and the plane-wave basis set. The size of the basis set in this case is controlled by the parameter called the kinetic energy cutoff for the wave functions. The convergence of the results in terms of the basis set size can be systematically studied by computing the total energy dependence on the kinetic energy cutoff shown in Fig. S1a. The convergence tests justify the kinetic energy cutoff for wavefunctions of 80 Ry.

Another important parameter is the discretization steps for the wave-vector grid (k-grid). This parameter affects the accuracy of the results related to the integrals over the Brillouin zone such as the charge density. The convergence tests suggest that the 4x3x1 works well for the supercell model (see Fig. S1b). The parameters derived for the supercell model represent the upper bound and work well for computations for the isolated Si and Tc slabs.

2. MBPT/GW parameters

The GW approximation for the Hedin equations implies the usage of the screened Coulomb potential. The screening model requires computing the dielectric matrix which, in turn, depends on the kinetic energy cutoff. In this work, using a series of MBPT for the Si/Tc supercell (see Fig. S2), we have estimated the value of this parameter to be 15 Ry.

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**FIG. S1.** Convergence of DFT parameters: a) the kinetic energy cutoff for wavefunctions and b) the wave-vector grid.

**FIG. S2.** Energy cutoff for the dielectric matrix
The computation cost for the self-energies depends on the convergence of the Coulomb-hole contribution with the number of unoccupied bands. In Fig. S3, we show the corresponding convergence tests for the conduction and valence band edges as well as for the band gaps. The convergence of the sums in the Coulomb-hole term can be improved (see Fig. S3a) using the modified static remainder approach proposed in [J. Deslippe et al., Phys. Rev. B 87, 165124 (2013)]. Note that this improvement is especially important for the band edges and related quantities such as ionization potentials and electron affinities. The convergence of the GW corrections for the band gaps is usually faster (see Fig. S3b).

FIG. S3. Convergence of the Coulomb-hole contribution to the GW corrections with the number of bands for the supercell model for a) the conduction and valence band edges and b) band gaps. The results have been obtained with (solid lines) and without (dashed lines) the modified static remainder approach. The blue color corresponds to the results for Tc, the black color denotes Si.

FIG. S4. Convergence of the Coulomb-hole contribution to the GW corrections with the number of bands for the conduction and valence band edges for a) the isolated Tc slab, b) the isolated Si slab and b) bulk silicon. The results have been obtained with (solid lines) and without (dashed lines) the modified static remainder approach.

The convergence tests for the supercell model set the upper bound for the parameters. For the smaller systems, the requirements to the parameters can be relaxed. In Fig. S4, we show the dependence of the Coulomb-hole contribution on the number of bands for GW computations for the isolated Tc slab, isolated Si slab and bulk silicon used in the line-up potential method. In all these cases, convergence has been achieved faster as compared to the supercell model.

3. DFT band structure

The data in Fig. S5 compares the band structure for the Si/Tc supercell and isolated slabs. The colour in the figures denotes the projections of the states on boxes confining the silicon and first and second layers of tetracene.
FIG. S5. Band structure obtained within DFT for a) the supercell model, b) isolated Tc slab and c) isolated Si slab