Charge-transfer states and optical transitions at the pentacene-TiO$_2$ interface

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Abstract

Pentacene molecules have recently been observed to form a well-ordered monolayer on the (110) surface of rutile TiO$_2$, with the molecules adsorbed lying flat, head to tail. With the geometry favorable for direct optical excitation and given its ordered character, this interface seems to provide an intriguing model to study charge-transfer excitations where the optically excited electrons and holes reside on different sides of the organic–inorganic interface. In this work, we theoretically investigate the structural and electronic properties of this system by means of ab initio calculations and compute its excitonic absorption spectrum. Molecular states appear in the band gap of the clean TiO$_2$ surface, which enables charge-transfer excitations directly from the molecular HOMO to the TiO$_2$ conduction band. The calculated optical spectrum shows a strong polarization dependence and displays excitonic resonances corresponding to the charge-transfer states, which could stimulate new experimental work on the optical response of this interface.

1. Introduction

Investigations on hybrid organic–inorganic systems [1–8] have opened up the possibility to combine the benefits of both constituents and devise new applications that outperform their either purely organic or inorganic counterparts. For example, the possibilities of tailoring the electronic band structure can be considerably extended compared to inorganic heterostructures, because the organic molecules can more flexibly adjust to the underlying lattice of the inorganic substrate [9, 10]. The band structure of a hybrid system can be further tuned by modifying the properties of the organic material [1, 10]. Such hybrid systems can also provide new types of semiconductor excitations, like the hybrid Frenkel–Wannier exciton [11] with a high oscillator strength combined with an enhancement of nonlinear optical response [2, 12], or the hybrid charge-transfer exciton [5–8] where a bound electron–hole pair is formed with the electron and hole residing at different sides of the organic–inorganic interface of the system.

These ideas have already been applied in photovoltaics [10], where dye-sensitized solar cells [3, 13–17] have been found to be promising in the search for efficient, low-cost, and environmentally friendly devices. The operational principles of solar cells are fundamentally dependent on charge-transfer excitations at the interfaces between the two constituents [5–8]. Even though charge-transfer excitations have been intensively studied during the last decades [5–8, 18–22], the charge-transfer nature of the excited states [5, 8, 23] is not well understood. In order to enhance the performance of photovoltaic devices, it is especially important to characterize the mechanisms involved in the formation [5, 23] and dissociation [5, 6] of such excitons [8]. Therefore, it is desirable to study systems where the charge-transfer interface-excitation states are strongly identifiable, e.g., in the optical spectrum. Such model systems could reveal the fundamental character of the charge-transfer states through clearly visible features in the optical spectra.
In many dye-sensitized solar-cells, organic molecules with good light-absorbing properties are placed in contact with porous TiO₂ [3, 13, 14], with the effect that a photocurrent can transfer an electron from the molecule to the TiO₂ conduction band. Pentacene is a π-conjugated molecule, and it acts as an electron donor in bulk-heterojunction cells [24] when combined with fullerene or their functionalized derivatives, such as PCBM [24]. Also its use in dye-sensitized solar cells has been reported [17]. When pentacene adsors at semiconductor or insulator surfaces, such as SiO₂, it is usually almost upright [25], making the π-orbitals pointing parallel to the surface. However, recently pentacene has been shown to adsorb lying down on a rutile TiO₂(110) surface for a coverage up to 3 monolayers, as was deduced by STM and x-ray absorption measurements [26]. In this configuration, the overlap between the π-orbitals of the molecule and the substrate states is increased, which may increase the interaction strength between the carriers of different constituents. Consequently, the pentacene monolayer on TiO₂ might provide a prototypical system where charge-transfer excitations between the molecule and the surface can take place directly upon optical excitation, enabling in-depth studies of these excitations from the related spectra. Furthermore, experiments [26] indicate that pentacene molecules form a very well-ordered wetting layer on rutile TiO₂(110), providing a well-defined organic–inorganic interface, making it an ideal candidate for theoretical studies, in contrast to other similar interfaces that show very complex and disordered structures.

In modeling molecules adsorbed on surfaces, density functional theory (DFT) often produces geometries and ground state electronic properties with sufficient accuracy. As extensions, many-body techniques such as the GW approximation together with the Bethe–Salpeter equations (BSE) [27, 28] can access the quasiparticle band energies and linear response spectra, while one can apply, e.g., the cluster–expansion approach [29, 30] to fully include the nonlinear [31] and nonequilibrium [32, 33] many-body kinetics using the semiconductor Bloch equations [34] (SBE) and their extensions [35]. These methods require the electronic band energies together with matrix elements for light–matter and Coulomb interactions, including the dielectric screening, as an input. These can be obtained from ab initio calculations, from experimentally deduced parameters, or from a combination of both [36].

In this work, we model the pentacene monolayer on TiO₂(110) using DFT and compute the linear response optical spectrum with the BSE for a set of system Hamiltonians similar to those frequently used in conjunction with the BSE method (that is, using screened direct and unscreened exchange interactions). We summarize the SBE extension of the approach briefly in the appendix. We generate the system Hamiltonians from ab initio data with an additional and varying parameterization of the dielectric screening, allowing us to study the changes in the nature of the dominant optical excitations as the effectiveness of the electronic screening provided by the substrate changes. We find that there are optical charge-transfer excitations between the pentacene molecule and the TiO₂ surface and demonstrate that the system is promising for studying properties of hybrid charge-transfer excitons, especially, their unusual symmetries and polarization dependence.

2. Methods

To determine the geometry of the system, we optimize it using the SIESTA DFT code [37]. We use a slab geometry with a 1 × 6 supercell (with respect to the primitive surface unit cell) in the surface plane, and five layers of TiO₂ in the direction perpendicular to the surface. In total, we have 216 atoms in the unit cell and use 20 Å of vacuum in order to minimize the interactions between periodically repeated slabs. To include van der Waals contributions to the energy and forces, we employ the optB88 functional [38]. Our double-ζ polarized (DZP) basis set of numerical atomic orbitals is generated using an energy-shift parameter of 100 meV (see [37] for a detailed explanation of these parameters), and the core electrons are replaced by Troullier–Martins pseudopotentials [39]. Starting from the DFT results, we obtain the relevant band structure and wave functions to compute all the quantities that we need to set up and solve the BSE, as described below.

2.1. Excitonic resonances in optical spectra

An exciton consists of a Coulomb-bound electron–hole pair [29] that can be described, e.g., by the two-particle Green’s function. Here, we analyze excitonic resonances in linear absorption by applying the standard BSE approach [27, 40]. Technically, we solve an eigenvalue problem

\[ H^{\text{BSE}} A = \epsilon A \]

for the effective BSE Hamiltonian

\[ H^{\text{BSE}}_{\text{mkk,nm'k'}} = (\epsilon_{\text{mk}} - \epsilon_{\text{nk}}) \delta_{\text{mm'}} \delta_{\text{nn'}} \delta_{\text{kk'}} + (f_{\text{mk}} - f_{\text{nk}}) K_{\text{mkn,nm'k'}} \]
where $\epsilon_{nk}$ is the quasiparticle energy of an electron in band $n$ with crystal momentum $\mathbf{k}$ and $f_{nk}$ is the electronic occupation. A scissor operator can additionally be introduced for $\epsilon_{nk}$ without any loss of generality. The Coulomb kernel

$$K_{nmk,n'm'k'} = 2 \int d^3r \int d^3r' \psi_{nmk}^*(\mathbf{r}) \psi_{n'm'k'}^*(\mathbf{r}') \mathbf{v}(\mathbf{r}, \mathbf{r}') \times \psi_{n'k'}(\mathbf{r}') \psi_{nmk}(\mathbf{r}),$$

\begin{equation}
\times W(\mathbf{r}, \mathbf{r}') \psi_{nmk}^*(\mathbf{r}) \psi_{n'k'}(\mathbf{r}),
\end{equation}

contains quasiparticle wave functions $\psi_{nk}$ as well as the bare ($v$) and screened ($W$) Coulomb interactions. The first term in (3) is the repulsive exchange contribution (with the factor of two appearing for the optically relevant singlet excitation) and the second is the attractive direct term; the one responsible for excitonic binding.

We construct the linear optical absorption from the imaginary part of the macroscopic dielectric tensor $\varepsilon_M^{ii}(\omega)$ in different Cartesian directions $i$, following the procedure in [27, 28]. In practice, we make use of the representation

$$\varepsilon_M^{ii}(\omega) = 1 - 4\pi \sum_{nmk} D_{nmk}^ii \rho_{nmk}^i(\omega),$$

where the density-change matrix $\rho_{nmk}^i(\omega)$ reads

$$\rho_{nmk}^i(\omega) = \frac{1}{V} \sum_{\lambda\lambda'} \sum_{n'm'k'} A_{nmk}^{\lambda\lambda'} S_{\lambda\lambda'}(\omega - \epsilon_{nk} - i\gamma) D_{n'm'k'}. \quad (5)$$

Here $V$ is the volume of the supercell (or quantization volume) related to the sampling of the Brillouin zone and $S_{\lambda\lambda'} \equiv \sum_{nmk} A_{nmk}^{\lambda\lambda'} A_{nmk}^{\lambda\lambda'}$ defines the overlap between the (right) eigenvectors. In (4) and (5),

$$D_{nmk}^i = \frac{i}{\epsilon_{nk} - \epsilon_{nk}} \int d^3r \psi_{nmk}^*(\mathbf{r}) \mathbf{p}_i \psi_{nmk}(\mathbf{r}),$$

are the dipole matrix elements with $\mathbf{p}_i$ the momentum operator in Cartesian direction $i$ and the $\sqrt{2}$ factor appears for a singlet exciton [40]. When non-local pseudopotentials are used to compute the wave functions a correction to the matrix elements of $\mathbf{p}_i$ should also be included [41, 42]. Note that the energies in the denominator in (6) should not be modified when a scissor operator is used.

In the Tamm-Dancoff approximation [27] (TDA) where particle–hole pairs are assumed to be uncoupled from the hole–particle pairs the solutions of (1) have the meaning of expansion coefficients of an exciton wave function

$$\psi^i(\mathbf{r}, \mathbf{r}') = \sum_{\nu c} A_{\nu c k}^i \psi_{\nu c k}(\mathbf{r}) \psi_{nmk}^*(\mathbf{r}'),$$

where indices $\nu$ and $c$ denote occupied and unoccupied states, respectively.

### 2.2. Computational aspects of the spectrum calculations

We solve the equations above numerically using a set of newly developed codes that act as post-processing tools for the SIESTA code. In our numerical solutions we approximate the quasiparticle wave functions $\psi_{nk}(\mathbf{r})$ as the DFT Kohn–Sham solutions; an approximation commonly used in GW/BSE calculations. We take the band energies $\epsilon_{nk}$ to be the Kohn–Sham eigenvalues modified by a scissor operator to open up the band gap, as explained in detail later. In practice, the matrix elements of the DFT Hamiltonian are imported from SIESTA in a basis of local atomic orbitals and are rediagonalized to obtain wave functions and band energies for all relevant $\mathbf{k}$-values. We modified the SIESTA code to export momentum matrix elements in the local basis, including the corrections due to the use of non-local pseudopotentials. These are subsequently imported and converted to the eigenstate representation to be used in (6).

The Coulomb integrals in (3) are computed by making use of a real space grid inside the unit cell and its corresponding plane wave expansion. For a given plane wave cutoff energy the number of grid points in real space as well as in reciprocal space is determined automatically and one can go between the two representations via Fourier transforms. First, the periodic part of the wave functions, which at this point are expanded in localized orbitals, are converted to the real space grid representation, then the electrostatic potential originating from each product state, e.g., $v_{nmk,m'k'}(\mathbf{r}) \equiv \int d^3r \mathbf{v}(\mathbf{r}, \mathbf{r}') \psi_{nmk}(\mathbf{r}) \psi_{n'm'k'}^*(\mathbf{r}')$ is solved by going to reciprocal space where the Coulomb interaction is diagonal. After a back transform to real space, the potential is multiplied with the other product state on the grid and integrated, e.g., $\int d^3r \psi_{nmk}(\mathbf{r}) \psi_{n'k'}(\mathbf{r}) \psi_{nmk,m'k'}^*(\mathbf{r})$. We use a 2D-truncated Coulomb interaction [43, 44], with the spatial cutoff set to half the cell in the normal direction. The Coulomb singularities are treated by replacing each diverging contribution with its numerical average over a small volume in $k$-space (defined by the original $k$-mesh) around the divergent point [44]. The averaging is performed using an auxiliary $10 \times 10 \times 10$ Monkhorst-Pack $k$-mesh centered at, but excluding, the divergent
point. A plane wave cutoff of 300 eV is used (differences to computed spectra with 600 eV are verified to be negligible).

The electronic part of the dielectric screening can, in principle, be approximately modeled *ab initio* using the random phase approximation. However, such a procedure would be numerically extremely costly because our unit cell is so large. Furthermore, it has been suggested [28, 36] to computer contributions from phonon modes in bulk TiO₂ can be important for the effective dielectric function necessary to properly describe the lowest lying excitons. Rutile TiO₂ has a large difference between the purely electronic screening ($\varepsilon_{\infty, ||} = 8.43$, $\varepsilon_{\infty, \perp} = 6.84$) and the static one where also the nuclei can relax ($\varepsilon_{\parallel} = 257$ and $\varepsilon_{\perp} = 111$). A good agreement with TiO₂ experiments in bulk was found [36] by using $\varepsilon = 47.8$ (now geometrically averaged over the directions) to compute excitonic absorption.

In our interface-dominated system the dielectric behavior will be strongly modified from that of the bulk. A simple estimate produces a dielectric constant for $q$ approaching zero that is an average of bulk TiO₂ and vacuum [46], yielding $\varepsilon = 4.2$ if the directionally averaged $\varepsilon_{\infty}$ is used, or $\varepsilon = 24.4$ when taking the best fit value above [36]. In [47] an image charge model was used to fit the dielectric constant for a molecule adsorbed above a TiO₂(001) surface, with the best fit given by $\varepsilon = 2.76$, which is lower than the estimate above. These limiting cases indicate the range of the expected $\varepsilon$ as the screening changes locally across the TiO₂-pentacene interface.

Since computing the screening microscopically is presently extremely challenging for such a large system, we model it by an effective dielectric constant over the reasonable range. Specifically, we explore three models where the dielectric constant is set to a low ($\varepsilon_1$), middle ($\varepsilon_2$) and high ($\varepsilon_3$) value. For the low and high values, we choose the two averaged values of the TiO₂ bulk and vacuum discussed above, that is $\varepsilon_1 = 4.2$ and $\varepsilon_3 = 24.4$ respectively. The middle value of $\varepsilon_2 = 7.2$ is chosen to give the average binding energy of $\varepsilon_1$ and $\varepsilon_3$, assuming the binding energy to be $\propto 1/\varepsilon$ as is the case for a two-state system using (2).

### 3. Results and discussion

The geometry is optimized by keeping the middle TiO₂ trilayer frozen while letting all other atoms, including the molecule, relax. The lattice constant in the in-plane direction is fixed to the optimized bulk value obtained with the same functional and basis set ($a = 4.60$ Å, $b = 2.98$ Å), giving a surface $1 \times 6$ unit cell of $a = 6.51$ Å and $b = 17.87$ Å. The geometry is schematically shown in figure 1 where gray denotes Ti atoms, red O, blue C, and white H. The pentacene molecule is adsorbed over the surface, tilted inwards to the troughs formed by the Ti–O rows on the TiO₂ (110) surface with an angle of 24°, in agreement with the experimentally deduced 25°. The closest C–Ti distance is 2.76 Å and the closest C–O distance (coming from an oxygen row) is 2.86 Å.
3.1. Band structure and projected density of states (PDOS)

For the geometry described above, figure 2 presents the computed band structure as well as the PDOS for the different atom species, both for the bare surface (upper frames) and the surface with the adsorbed molecules (lower frames). The high symmetry points in reciprocal space are, in units of the reciprocal lattice vectors, \( \Gamma = (0, 0, 0) \), \( X = \left(0, \frac{1}{2}, 0\right) \), \( M = \left(\frac{1}{2}, \frac{1}{2}, 0\right) \), and \( X' = \left(\frac{1}{2}, 0, 0\right) \). As the basis vectors of the unit cell are orthogonal, the reciprocal unit vector directions correspond to those of the real lattice shown in figure 1.

Comparing the surface with and without the molecule shows that the surface bands are almost unaffected by the adsorption, except for the appearance of two flat bands in the band gap that are both situated below the Fermi level. Also the lowest conduction band comes down slightly, while still being almost degenerate with another band between the high-symmetry points X and M.

To assign the bands we take a look at the PDOS. The two gap states below the Fermi level mostly have contributions from the carbon atoms, that is, they belong to the pentacene molecule. The first unoccupied bands, however, belong mostly to the slab and have predominant contribution from Ti 3d orbitals. Indeed, this part of the band structure is very similar to the one coming from the bare surface, without the molecule, so the effect of the molecule on these bands seems to be small. The lowest unoccupied band is seen to be delocalized through the whole slab, so even though it has contributions from the surface atoms it is not a pure surface state. Higher up in energy, we see the contributions from the unoccupied pentacene states, centered at around 0.5 eV above the lowest surface conduction band, with the lowest weak feature at 0.25 eV above the same. The combination of well-separated molecular occupied states and low-lying unoccupied states belonging to the substrate suggests the possibility of optical charge-transfer excitations from the molecule to the surface where the unoccupied molecular states are not expected to contribute much.

3.2. Band alignment

It is well-known that the band alignment can sometimes be a problem in DFT calculations for molecules on surfaces due to an unbalanced description of the different constituents. To investigate whether or not DFT qualitatively gives the correct band alignment for our system we look at a simple two-step procedure that has been successfully used to align molecular levels for surface adsorbates on metal and semiconductor surfaces [47–49]. In the first step individual shifts for the levels are computed in separate calculations for the bare substrate and the gas phase molecule. In the second step an image charge model is used to include the additional screening provided by the substrate that modifies the molecular electron removal and addition energies. In this...
way individual shifts for the substrate and molecular level are obtained, which can later be applied to the combined molecule-substrate DFT calculation to align the bands.

In order to obtain an unbiased description of the levels of the molecule and the surface we use (the negative of) the experimental ionization potentials and electron affinities as reference values. For the bare substrate, experimentally deduced values are in the range $-8.5$ to $-8.7$ eV for the highest valence band and $-5.2$ to $-5.4$ eV for the lowest conduction band [50]. The DFT-computed values (related to the vacuum level) for the bare surface are $-6.95$ and $-5.76$ eV, resulting in shifts of $-1.55$ eV ($-1.75$ eV) and $0.56$ eV (0.36 eV), with the lower experimental values in parenthesis. For pentacene in the gas phase the experimental values are $-6.63$ eV and $-1.39$ eV for HOMO and LUMO respectively [51]. From DFT we obtain $-4.61$ and $-3.34$ eV, which results in a shift for the first step of $-1.99$ and $1.95$ eV. In the second step we add the image charge correction to the shift for the molecular levels. The image charge model shifts occupied (unoccupied) states by $\Delta E_{\text{oc}} = - \Delta E_{\text{unoc}} = - q q / \left(4 (z - z_0)\right)$, in atomic units, where $q$ is the electronic charge, $q = (1 - \epsilon) / \left(1 + \epsilon\right)$ is the screened image charge, $z$ is the height of the molecule above the surface and $z_0$ is the position of the image plane. To determine $z_0$ we fit $\Delta E_{\text{unoc}}$ to match the exchange-correlation potential for the TiO$_2$ surface [47–49], giving us a plane $0.25$ Å above the oxygen rows. We use the directionally averaged experimental $\epsilon_\infty$ for bulk TiO$_2$, that is $\epsilon = 7.4$, and consider the pentacene molecule to be located $2.8$ Å above the surface, resulting in a shift of $\pm 1.08$ eV. The image charge correction reduces the shift for the molecular levels to $-0.92$ eV and $0.87$ eV for HOMO and LUMO, respectively.

Applying these shifts to the DFT band structure, as seen in figure 2, we see that the molecular HOMO is still in the band gap of the surface and the molecular LUMO is shifted up in energy in relation to the surface conduction band edge. In other words, our two-step procedure predicts that the lowest excitations will be from the molecule to the surface, as the DFT band structure suggests, with little influence of the molecular LUMO that has a much higher energy. We also note that the band gap between the molecular HOMO and the conduction band edge has opened up from $0.55$ to $2.02$ eV ($1.82$ eV) where the value in parenthesis refers to the lower value used for the experimental reference. Furthermore, the corrected band gap shows a relative insensitivity to the dielectric constant that enters in the image charge formula; if the bulk $\epsilon_0$ would instead be used (close to full screening) the value of the gap would be only $0.32$ eV lower. In light of this, we feel justified in using the DFT band structure in the optical calculations, only opening up the band gap with a scissor operator.

3.3. Optical absorption and polarization dependence

All optical spectra are computed using one fully occupied band $v_1$ and five unoccupied bands $e_1$–$e_5$ with a $55 \times 19 \times 1$ Monkhorst-Pack $k$-mesh spanning the whole Brillouin zone (BZ). We use a scissor operator of $1.47$ eV that gives a fundamental gap in our system (from the molecular state in the gap to the lowest conduction band) of $2.02$ eV, in accordance with the higher value from our model for the band alignment. This estimate cannot be fully checked due to absence of experimental data. However, the exact value of the gap will not influence the relative positions of optical resonances within the TDA. Our results verify that this approximation gives visually identical spectra compared with the full solution of (1). For an easier interpretation, we discuss the TDA results in the remainder of this paper.

The computed linear absorption spectrum $(\chi \text{Im} [\varepsilon_M^\mu(\omega)])$ is shown in figure 3 for the three model dielectric functions, together with the non-interacting spectrum. The purple, blue, and orange areas correspond to response in $x$-, $y$-, and $z$-polarization direction, respectively. We observe that the Coulomb interaction changes all the spectra substantially, giving also a high sensitivity to the screening model used. In other words, the actual $\epsilon$ should be directly deducible from absorption experiments.

While the quantitative spectra vary drastically as a function of $\epsilon$, some qualitative features remain $\epsilon$-independent. For example, the spectra exhibit a strong dependence on polarization direction, to a degree that different directions contain different resonances. This is seen most clearly for $e_1$ and $e_2$, producing three separate excitonic resonances labeled A, B, and C. The lowest energy resonance A is clearly visible only for the $z$-polarized light while the B resonance is connected with the $y$ polarization. The resonance C dominates the spectrum for the $x$ and $z$ polarizations, but practically vanishes for the $y$ polarization. All resonances A, B, and C indicated in figure 3 originate from individual excitonic states. In the noninteracting system, by definition, we do not have excitonic resonances, but nevertheless even in this case the similar spectral regions corresponding to A, B, and C resonances are detectable, as shown in the lowest frame of figure 3.

3.4. Average hole and electron positions

For a given exciton, the averaged density of the electron and the hole follow from

$$
\rho_\lambda^\mu(r') = \int d^3 r \, |\Psi^\lambda(r, r')|^2 = \frac{1}{V} \sum_{\nu \omega k} A_{\nu \lambda k}^* A_{\omega \lambda k}^* u_{\nu k}(r') u_{\omega k}^*(r'),
$$
respectively. The lattice-periodic part, \( u_{\mathbf{k}}(\mathbf{r}) \), of the Bloch function guarantees that \( \rho_{\mathbf{e} \mathbf{h}}^{\lambda}(\mathbf{r}) \) is also lattice periodic. This periodicity stems from the average over the spatial distribution of one of the carriers, either the electron or hole. For a single electron–hole excitation, \( \rho_{\mathbf{e} \mathbf{h}}^{\lambda}(\mathbf{r}) \) is just the absolute square of the unoccupied Bloch wave function.

Figure 4 shows the regions of high \( \rho_{\mathbf{e} \mathbf{h}}^{\lambda}(\mathbf{r}) \) and \( \rho_{\mathbf{h}}^{\lambda}(\mathbf{r}) \) over the surface plane direction, and their projection (left axis) as a function of the \( z \)-coordinate, for the \( \epsilon_1 \) model. The hole distribution corresponds to the molecular HOMO and is relatively unchanged for different transitions, so we only plot the one for the A transition. The corresponding \( \rho_{\mathbf{e} \mathbf{h}}^{\lambda}(\mathbf{r}) \) isosurfaces are shown for A, B, and C transitions. The A and B excitons yield visually almost identical distributions because they essentially originate from the same unoccupied band \( c_1 \), although for different \( \mathbf{k} \)-values and symmetries in the Brillouin zone, as will be discussed later in more detail. However, the C excitons mainly stem from the \( c_2 \) band, and although higher in energy, it has part of the density closer to the molecule and consequently has more overlap with the hole state. This partly explains the higher absorption peak in figure 3.

3.5. Band mixing in excitonic resonances

To characterize the spectral features seen in figure 3, we first separate the different contributions to the spectra by using only one conduction band at a time in the sum (4). Figure 5 shows this separation for the \( \epsilon_1 - \epsilon_3 \) band contributions in the polarization-averaged absorption for \( \epsilon_1 - \epsilon_3 \), as well as for the noninteracting case. In the noninteracting case, each eigenvector \( A^\lambda \) is connected to one conduction band only, but when the Coulomb interaction is included the transitions become mixed, i.e., \( A^\lambda \) will contain contributions from several \( \epsilon_n \). In this case, even when only one \( \epsilon_n \) is considered in the sum of (4), the related density-change-matrix element \( \rho_{\epsilon_n \mathbf{k}}^{\lambda}(\omega) \)
will include contributions from other conduction bands than \( \epsilon_n \). Thus, the contributions of different bands to the spectra can be exactly disentangled by the used approach only in the noninteracting case, while the separation is only approximative when the Coulomb interaction is fully included. The Coulomb-induced mixing of transitions also results in some negative spectral features in the decomposition as seen in the interacting cases of figure 5. Nevertheless, the shown results give a good general picture of which \( \epsilon_n \) bands the A, B and C resonances are most closely connected.

For the noninteracting case, we see that the A and B regions in the absorption originate from \( \epsilon_1 \) contributions while the C region comes predominantly from \( \epsilon_2 \). The same holds for \( \epsilon_3 \) which has a large enough screening for the bands not to mix in \( A \) appreciably due to the Coulomb interaction. We observe that \( \epsilon_1 \) and \( \epsilon_2 \) yield similar trends, while making \( \epsilon_3 \) smaller enhances mixing of transitions such that eventually all bands contribute to all excitonic resonances.

### 3.6. Excitonic states at the interface

To identify the \( \mathbf{k} \) dependence of excitons one would optimally plot \( A_{nmk}^\Delta \) and \( D_{nmk}^\epsilon \) as functions of \( \mathbf{k} \). However, when taken directly from our DFT-based results, both of these contributions may contain arbitrary phase jumps in \( \mathbf{k} \), due to the ‘gauge-freedom’ [52] problem, i.e., the freedom in choosing the phases of \( \psi_{\mathbf{k}n} \). Additionally, as \( \mathbf{k} \) is generally a state index rather than an actual wave-vector coordinate, there is no need of \( A_{nmk}^\Delta \) and \( D_{nmk}^\epsilon \) being continuous functions of \( \mathbf{k} \), even without the phase jumps. Indeed, \( \psi_{\mathbf{k}n}(\mathbf{r}) \) can become discontinuous in \( \mathbf{k} \) at band intersections [53, 54]. This complicates visualization, especially, when ‘band-mixing’ [55] is significant, i.e., when \( | \langle \psi_{\mathbf{k}n}| \psi_{\mathbf{k}m} \rangle |^2 \) differs considerably from unity between \( \mathbf{k} \) and \( \mathbf{k}' \) in immediate vicinity but on opposite sides of the intersection, for all choices of \( n \) and \( m \). Such band-mixings are expected to be important for large unit cells due to effects of band folding with respect to the bands for the bulk and/or primitive surface unit cells.

Since \( \psi_{\mathbf{k}n} \) and \( \epsilon_n \) are energetically isolated, they are not affected by the above band-mixing, yielding a continuous \( D_{\epsilon n\mathbf{k}}^\epsilon(\mathbf{r}) \) after matching the phases between \( \mathbf{k} \) states. In fact, our diagonalization scheme produces

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**Figure 4.** The average electron and hole positions for \( \epsilon_1 \), as isosurfaces and averaged over the \( x, y \) as a function of \( z \). Upper left: the average hole position, for transition A, as a function of \( z \) is shown in blue and its corresponding isosurface in the representation of the unit cell next to it. Upper right: the average electron position for the A transition and its corresponding isosurface are shown in purple. Lower left and right: the same for the B and C transitions. The dashed lines represent the borders of the TiO\(_2\) slab.
and \( \epsilon = 2 \) and set it to be positive-valued quantity at the \( \Gamma \)-point. After this step, SIESTA yields continuous \( v_1 \leftrightarrow \epsilon_1 \) dipoles that fulfill \( \text{Im}[D^\epsilon_{11;11}'] = 0 \) and \( D^\epsilon_{11;11} = (D^\epsilon_{11;11})^\ast \).

We apply the sign convention, obtained above from \( D^\epsilon_{11;11} \), to the signs of \( A^\lambda_{\gamma n;\mathbf{k}} \). Additionally, we select the phase of the excitonic state such that \( \text{Im}[A^\lambda_{\gamma n;\mathbf{k}}] = 0 \). As a result of these procedures, also \( A^\lambda_{\gamma n;\mathbf{k}} \) becomes continuous and \( A^\lambda_{\gamma n;\mathbf{k}} = (A^\lambda_{\gamma n;\mathbf{k}})^\ast \) is fulfilled. In this system, \( \epsilon_2 - \epsilon_5 \) bands exhibit so strong band mixing that following exciton through only one of these bands is not useful. Therefore, we investigate an effective exciton distribution

\[
\phi^\lambda_k \equiv \left[ \sum_{\mathbf{G}} |A^\lambda_{\gamma n;\mathbf{k} + \mathbf{G}}|^2 \right]^{1/2},
\]

which is insensitive to the phase and band-mixing issues. Mathematically, \( |\phi^\lambda_k|^2 \) corresponds to the absolute square of the Fourier transform of \( \epsilon \) that is summed over all reciprocal lattice vectors \( \mathbf{G} \), i.e., \( |\phi^\lambda_k|^2 = V^{-2} \sum_{\mathbf{G}} |\psi^\lambda(\mathbf{G} + \mathbf{k}, \mathbf{G}' + \mathbf{k})|^2 \).

The four upper rows of figure 6 show \( \text{Re}[A^\lambda_{\gamma n;\mathbf{k}}] \) (left), \( \text{Im}[A^\lambda_{\gamma n;\mathbf{k}}] \) (middle), and \( \phi^\lambda_k \) (right) for \( \epsilon_1 \) and \( \epsilon_5 \) excitons of A [(a)–(f)] and B [(g)–(l)] resonances. Figures 6(m) and (n) present \( \phi^\lambda_k \) for the C-resonance excitons of \( \epsilon_1 \) and \( \epsilon_5 \), respectively. Each frame is centered at \( \mathbf{k} = X' \) that is denoted by a filled circle in the center of each frame.

The A excitons are centered at X' with a predominantly even (real) \( s \)-like part in the Brillouin zone while having also an odd (imaginary) \( p \)-like part. The odd part contains from 40% (\( \epsilon_1 \)) to 80% (\( \epsilon_5 \)) of the weight in the total \( A^\lambda_{\gamma n;\mathbf{k}} \). The \( \epsilon_1 \) B exciton (frames (g)–(i)) shows even symmetry (60% of the weight in \( A^\lambda_{\gamma n;\mathbf{k}} \)) and resembles a \( s \)-like state at M-point while having a sizable odd (40%) contribution located at X' (or at M). The B state changes drastically when \( \epsilon \) is increased to \( \epsilon_5 \) (figure 6(j)), because the even fraction is only 20% and \( \text{Re}[A^\lambda_{\gamma n;\mathbf{k}}] \) has a \( d \)-like symmetry located at X'. At the same time, its \( p \)-like features centered at X' are strongly increased (figure 6(k)).

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**Figure 5.** The band decomposition of the directionally averaged macroscopic dielectric function using various values of the screening parameter \( \epsilon \). We have \( \epsilon_1 = 4.2, \epsilon_2 = 7.2, \epsilon_3 = 24.4 \), and the noninteracting results (from top to bottom). The colors of the total, and the different conduction band contributions, \( \epsilon_1 \) to \( \epsilon_5 \) are shown in the key of the figure.
The C states experience strong band mixing, and we analyze only $k_f$ figures 6 (m)–(n). These C excitons have even symmetry (more than 80% of the weight in $A_{V_{C,k}}^4$) and are predominantly s-like states centered at $X'$. The major contribution to these states at different $k$ comes from the $c_1$-band $u_{c_1,k}(r)$ that most resembles $u_{c_1,k}(r)$ at $k = X'$ (with respect to $|\langle u_{c_1,k} | u_{c_1,X}\rangle|^2$).

Figure 6. Exciton eigenvectors and effective exciton distributions in the BZ. Each frame is centered at the $X'$ point (filled circles in centers of frames). The $r_1$-band (a), and (b) odd contributions of the $r_1$, screening $A$-exciton state. In (c), the effective exciton distribution for the $A$ exciton of $r_1$, (d)–(f) show the same results for the $r_2$ A state, (g)–(i) for the $r_1$ B state, and (j)–(l) for the $r_2$ B exciton. The effective exciton distributions for (m) $r_1$ and (n) $r_2$ C-resonance excitons are show at the bottom. The results in (e) and (f) are scaled up by multiplying with a factor of two and the results in frame (m) are scaled up with a factor of three.
This detailed analysis of states yield the following conclusions: a resonances stem predominantly from \(c_1\)-band \(s\)-like excitons located at the \(X'\) point and the C resonance from predominantly \(s\)-like \(c_2\)-band states at \(X'\), independently of \(\epsilon\). However, the B-resonance changes its nature from a predominantly \(c_1\)-band \(s\)-like state at \(M\)-point to a \(c_1\) \(p\)-like state at \(X'\) between \(\epsilon_i\) and \(\epsilon_j\), respectively.

### 3.7 Combined symmetries of excitons and dipoles

Since we have a highly asymmetric unit cell and large portions of the BZ need to be considered, schemes based on symmetries of the carrier states to evaluate optical strengths of excitons are not convenient. Instead, we directly study the combined properties of \(A^{\lambda}_{r,n,k}, D_{c,n,k}^x\), and \(D_{c,n,k}^y\), and the oscillator strength \(J_n = \sum_{mk} (A^{\lambda}_{mn,k})^2 D_{mk}^X\) to interpret the polarization dependence of the spectra in figure 3. The dipole \(D_{c,n,k}^1\) combines the effects of approximate symmetries of electrons and holes with their mutual overlaps, and in \(J_n\), only the even-even and odd-odd, \(Re[\lambda]|Re[D]|\) and \(Im[\lambda]|Im[D]|\) respectively, contribute. Thus, it is sufficient to only compare the symmetries and magnitudes of only either real and imaginary parts of \(A^{\lambda}_{r,n,k}\) and \(D_{c,n,k}^x\) simultaneously.

Figure 7 shows the dipole matrix elements for \(n_1\) to \(c_1\) transitions. By comparing the real parts of the A excitons in figures 6(a) and (d) to the real parts of \(x\)- and \(y\)-directional dipoles in figures 7(a) and (b), we notice that \(Re[D_{c,n,k}^x]\) and \(Re[D_{c,n,k}^y]\) practically vanish at the \(X'\) region where the A-exciton contributions are centered. The imaginary parts of the A excitons (figures 6(b) and (e)) have similar symmetry as the imaginary part of \(x\)-directional dipole in figure 7(d). However, the magnitude of \(Im[D_{c,n,k}^x]\) is exceptionally small. Since \(Im[D_{c,n,k}^x]\) (figure 7(e)) and \(Im[A^{\lambda}_{r,n,k}]\) for A excitons (figures 6(b) and (e)) do not have similar symmetries, their contribution to \(J_n\) becomes negligible.

The mismatch in symmetries, difference in the \(k\)-space locations, and/or small magnitude of dipole for \(A^{\lambda}_{r,n,k}\) and \(D_{c,n,k}^x\) when \(i = x, y\), explain why the A resonances are not visible for \(x\) and \(y\) polarizations. In contrast, when we compare \(Re[A^{\lambda}_{r,n,k}]\) of A excitons (figures 6(a) and (d)) to \(Re[D_{c,n,k}^x]\) in figure 7(c) and \(Im[A^{\lambda}_{r,n,k}]\) (figures 6(b) and (e)) to \(Im[D_{c,n,k}^x]\) in figure 7(f), we notice the similarity (especially for \(\epsilon_j\)) between the symmetries and locations of the dipole and the exciton contributions. The found match makes the A resonances relatively well visible in the spectra for 2 polarization.

The same comparison as done above for the A resonance can be made for the B resonance in figures 6(g), (h), (j), and (k) with respect the dipoles of figure 7. This time, we find the match for \(y\)-polarization, explaining why the B resonance is optically active only for this particular polarization direction. (Especially \(Im[A^{\lambda}_{r,n,k}]\) in figures 6(h) and (k) matches \(Im[D_{c,n,k}^y]\) in figure 7(e).)

The \(Re[D_{c,n,k}^y]\) dipole-matrix-element contributions that corresponds best to the C resonance show many similarities with the \(c_1\) band dipoles in figures 7(a)–(c), with the exception that the dipole contributions for the C
resonance are shifted in the BZ so that the position of $X'$ and $Γ$ points are exchanged. In addition, the $x$- and $z$-directional dipoles for C resonances are roughly a factor of seven and a factor of two stronger than the $x$- and $z$-directional dipoles related to $e_1$ band. These remarks explain why the C resonance is visible for $x$ and $z$ polarizations, but is optically inactive for the $y$ polarization, and why the C resonances have a higher intensity compared to A resonances in figure 3.

4. Conclusions

We have modeled the pentacene overlayer of the rutile TiO$_2$(110) surface by DFT and computed excitons and optical spectra by solving the Bethe–Salpeter equation (BSE) for a set of physically motivated system Hamiltonians. Flat bands coming from the pentacene molecule are found in the band gap of the pristine surface, and the BSE solutions reveal excitations with charge-transfer character from the molecule to the surface. The optical spectrum shows a large sensitivity to the polarization direction which we explain by investigating the exciton solutions and transition dipole matrix elements in the Brillouin Zone (BZ) assigning the three dominant transitions by their approximate symmetries and locations in the BZ. Many qualitative features of the excitons are weakly dependent on the dielectric screening chosen in the system Hamiltonian, although the energetic positions of the peaks are more sensitive to the screening. An experimental characterization of the optical spectrum of such a well-defined organic/TiO$_2$ system will certainly help to get a deeper understanding on the dynamics of formation and decay of charge-transfer excitations at this technologically relevant interface.

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Appendix

In this work, we use the Bethe–Salpeter equation (BSE) to compute the optical spectrum starting from system Hamiltonians generated using the input from ab initio DFT calculations of the band structure and one-electron states. Having a reasonable system Hamiltonian to describe the system, an interesting alternative approach is to solve the semiconductor Bloch equations (SBE) [56], which would give almost identical (or identical) results in the linear regime, but opens the possibility to study nonlinear effects. Here we outline the similarities and differences between the two methods.

The BSE takes the form of linear response of the one-particle Green’s function with respect to an external perturbation while the SBE rely on the equation of motion for the microscopic polarization [29, 34]

$$ P_{\nu k} \equiv \langle \hat{\sigma}_{\nu k}^{\dagger} (t) \hat{\sigma}_{\nu k} (t) \rangle. $$

This quantity is equivalent to a particle–hole matrix element of the density matrix $\langle \psi k | \rho (\mathbf{r}, r', t) | c k \rangle$ or indeed that of the Green’s function $-i \langle \psi k | G (\mathbf{r}, t, r', t^+) | c k \rangle$ when the time argument $t^+$ is infinitesimally larger than $t$. In the BSE, the response of this matrix element determines the polarizability when the difference of the two time arguments in $G$ does not play any role, that is, when only a frequency-independent screening is considered in the equations. Thus, when using this standard approximation, the two approaches should be equivalent.

The optical spectrum in the BSE approach is usually computed from the $q \to 0$ limit of the dielectric function [27, 28], whereas in the SBE the response is determined via the macroscopic polarization $P(t) \equiv \sum_{\nu k} D_{\nu k} P_{\nu k} (t)$, where for notational simplicity we omit the polarization dependence. Since the SBE come from an equation of motion, it can be solved by time propagation and thus go beyond the linear response regime in several ways; strong fields that substantially change populations can be used, as well as multiple fields. In the linear response regime, the equations of motion can be reduced to an effective eigenvalue problem in the frequency domain which turn out to be equivalent to the corresponding effective eigenvalue problem of BSE in (1), when the standard approximations of diagonal quasiparticle states and statically screened interaction are employed.

The screening in BSE comes out naturally from the theory and requires the direct Coulomb interaction to be screened while the exchange Coulomb interaction should be bare, however for bulk systems the $G = 0$ component of the exchange interaction must be disregarded [27, 28] in order to solve for the macroscopic polarization.

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$^5$ Note that the indices become switched between $P_{\nu k}$ and the density matrix.
dielectric function $\varepsilon_M$ that gives the optical spectrum. In the SBE, usually both the exchange and direct terms are screened, using the rationale of a background dielectric constant coming from inactive electrons that do not contribute directly in the optical process [29, 36]. Since the screening in the SBE can be taken to be a parameter it can however also be chosen to coincide with the one of the BSE. In this case, the absorption coefficient $[29, 34]$ from SBE is proportional to the imaginary part of (4), i.e., to the results of figure 3.

In summary, the BSE and the SBEs are two approaches to the same problem that give very similar (or identical, when using the same approximations) results in the linear regime, while the latter has applicability also for nonlinear phenomena, and the choice to use one or the other depends on the problem at hand.

References

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