Modification of the Optical Properties of Molecular Chains upon Coupling to Adatoms

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Adsorbed atoms (adatoms) coupled to the matrix of solid state host materials as impurities can significantly modify their properties. Especially in low-dimensional materials, such as one-dimensional organic polymer chains or quasi-one-dimensional graphene nanoribbons, intriguing manipulation of the optical properties, such as the absorption cross section, is possible. The most widely used approach to couple quantum emitters to optical antennas is based on the Purcell effect. This formalism, however, does not comprise charge transfer from the emitter to the antenna, but only spontaneous emission of the quantum emitter into the tailored photonic environment, that is evoked by the antenna. To capture such effects, we present a tight-binding formalism to couple an adatom to a finite Su-Schrieffer-Heeger chain, where the former is treated as a two-level system and the latter acts as an optical antenna. We systematically analyze how the coupling strength and the position of the adatom influence the optical properties of the molecular chains in the model. We take into account charge transfer from the adatom to the antenna and vice versa via an inter-system hopping parameter, and also include Coulomb interaction within the antenna as well as between the adatom and the antenna. We show that coupling the adatom to one of the bulk atoms of the linear chain results in a substantial change in optical properties already for comparatively small coupling strengths. We also find that the position of the adatom crucially determines if and how the optical properties of the chains are altered. Therefore, we identify this adatom-chain hybrid system as a tunable platform for light-matter interaction at the nanoscale.

I. INTRODUCTION

The Su-Schrieffer-Heeger (SSH) model constitutes a simple yet powerful and instructive tight-binding (TB) based model to describe the electronic and topological properties of solids, and induced a large body of literature within the last four decades [1–13]. Besides being a playground to explore topological phases [6, 14] and quasiparticles [1, 15–17], it is also capable of revealing transport properties of organic polymers such as polyacetylene [18] and the electronic energy level diagrams of molecular chains, for instance, if applied to finite systems. Moreover, it is to a large extent analytically solvable and, therefore, allows for powerful conceptual insights into the underlying physical principles. Within the model, it can be readily decided if a given atomic chain is electronically conducting or acts as an insulator. Additionally, non-trivial topological phases and the appearance of near-zero energy edge states in finite chains can be investigated. All these features can be traced back to chains of atoms with only slightly different coupling constants that give rise to three fundamentally different systems: the linear atomic chain (conductor), the dimerized atomic chain (conventional insulator), and the topological insulator. These systems are physically realized in nature through several organic molecules. Linear polyenes, for instance, exhibit electrons that occupy $p_z$-orbitals of their hosting carbon atoms. Therefore, these molecules can be understood as a realization of a one-dimensional (1D)
We want to investigate the effect of introducing an electronically coupled adsorbed atom (adatom) into the TB description of the above-mentioned finite SSH chains. Coupling the adatom may result in symmetry breaking of the structure leading to a modification of its electronic properties and optical response [37]. Here, we aim to characterize the single-particle eigenstates of said Hamiltonian, and discuss the optical properties that follow from it in Sec. II. In Sec. III A, we investigate the stand-alone SSH chains without the adatom as a reminding preparatory work. Section III B focuses on the hybrid chain-adatom systems without Coulomb interaction, whereas in Sec. III C, we take into account electron-electron interaction before we summarize our findings in Sec. IV.

II. THEORY

We assume the hybrid system to consist of two components: a nanoscopic SSH chain that acts as an optical antenna and an adatom which is effectively described as a TLS. Both the adatom and the antenna are treated in a TB framework. In particular, we assume one mobile electron per carbon atom in the antenna’s p$_z$-orbitals $\{|l\rangle\}$ that are localized at r$_l$ in the vicinity of the corresponding host atoms $l \in [1, N_a]$ for an antenna of $N_a$ atoms. Mediated through π-bonds that connect p$_z$-orbitals of neighboring atoms $l$ and $l'$, electrons may change their location with a probability quantified by the TB hopping parameters $t_{ll'}$. They are proportional to the overlap integral of neighboring p$_z$-orbitals. For simplicity, we do not take into account the spin degree of freedom.

The TLS is characterized by its ground and excited states $|g\rangle$ and $|e\rangle$, representing two active orbitals of the adsorbed impurity with energies fixed at $E_g = -0.5$ eV and $E_e = 0.5$ eV relative to the isolated antenna’s energy levels. The adatom is coupled to one of the antenna’s carbon atoms only, as it is the case for hydrogen, fluorine, and hydroxyl groups as adatoms, for instance [49, 57]. The ground and excited states couple to the host atom in the antenna via hopping parameters $t_g$ and $t_e$.

A. Model Hamiltonian

The system Hamiltonian consequently reads

$$H = H_{\text{antenna}} + H_{\text{TLS}} + H_{\text{interaction}}$$

$$= - \sum_{l<l',|l|} t_{ll'} \left( |l\rangle\langle l'| + |l'|\langle l| \right)$$

$$+ E_e |e\rangle\langle e| + E_g |g\rangle\langle g|$$

$$+ t_e \left( |l_e\rangle\langle e| + |e\rangle\langle l_e| \right) + t_g \left( |l_c\rangle\langle g| + |g\rangle\langle l_c| \right),$$

(1)

where the atomic site indices $l, l'$ run over the antenna atoms, $\{l, l'\}$ denotes a pair of nearest neighbor atoms, and $l_c$ is the antenna’s atomic site the adatom is coupled to. We denote the $N = N_a + 2$ energy eigenstates of the hybrid system by $\{|j\rangle\}$, where $j \in [1, N]$ and

$$H|j\rangle = E_j |j\rangle.$$  

(2)

Here, the energies $E_j$ are given relative to the TB onsite energies which are set to zero in the Hamiltonian in Eq. (1). The energy eigenstates may be expanded into the complete and orthonormal real-space atomic site basis $\{|l\rangle\} \cup \{|g\rangle, |e\rangle\}$ according to

$$|j\rangle = c_{je}|e\rangle + c_{jg}|g\rangle + \sum_{l=1}^{N_a} c_{jl}|l\rangle.$$  

(3)
B. State Characterization

In the joint antenna-adatom system, the energy eigenstates of the stand-alone antenna and the ones of the adatom hybridize, making it difficult to identify the stand-alone modes. In this paper, it is our goal to determine the conditions under which the presence of the adatom considerably modifies the optical properties of the isolated antenna. We especially focus on the tunability of the chain modes. To achieve this goal, we put in place scalar measures for certain properties of the energy eigenstates that help to understand, quantify, and illustrate the changes that the electronic structures of the systems undergo. These measures map single-particle energy eigenstates to real numbers and, therefore, provide an intuitive manner to quantify their characteristics, which translate into optical properties, and to assign a physically meaningful order to them. The measures characterize the hybrid system for different parameter sets and especially for various coupling strengths and coupling positions. For the sake of brevity, from now on we use \{\{|l\}\} = \{|l\} \cup \{|g\}, \{e\}\} for the set of all real-space based active orbitals in the hybrid system.

1. State Localization

We introduce the localization \(L_{\langle j \rangle}\), a measure that quantifies how strongly state \(|j\rangle\) is localized on certain antenna sites \(|l\rangle\) or adatom orbitals \(|e\rangle\) and \(|g\rangle\),

\[
L_{\langle j \rangle} = \frac{(1 - p_{\langle j \rangle})}{N - 1} \in [0, 1],
\]

where the participation ratio \([58–61]\)

\[
p_{\langle j \rangle} = \left( \frac{\sum_i |c_{ji}|^2}{N \sum_i |c_{ji}|^4} \right)^2 = \left( N \sum_i |c_{ji}|^4 \right)^{-1} \in [1/N, 1]
\]

is a measure for the number of atomic site orbitals \(|l\rangle\) that are significantly involved in the spatial distribution of the energy eigenstate \(|j\rangle\) (the second equality in Eq. 5 holds for normalized states only). If the spatial distribution of state \(|j\rangle\) is uniform on all the sites in the system, i.e. \(c_{ji} = 1/\sqrt{N}\), then \(p_{\langle j \rangle} = 1\) and \(L_{\langle j \rangle} = 0\), and we call the state completely delocalized. For a state localized on a single site \(\mathbf{l}_0\), i.e. \(c_{ji} = \delta_{i0}\), we obtain \(p_{\langle j \rangle} = 1/N\) and \(L_{\langle j \rangle} = 1\), and consequently call the state fully localized.

2. State Hybridization

To measure how strongly an eigenstate of the stand-alone isolated antenna is disturbed and modified by the presence of the adatom, we introduce the hybridization \(h_{\langle j \rangle}\). It is defined as

\[
h_{\langle j \rangle} = 1 - |\langle j \| j^0 \rangle|,
\]

where \(|j^0\rangle\) is an energy eigenstate of the Hamiltonian Eq. (4) for \(t_c = t_0 = 0\) that evolves to \(|j\rangle\) when the coupling is turned on. Hence, in the completely decoupled system, we have \(|j\rangle = |j^0\rangle\) and \(h_{\langle j \rangle} = 0\ \forall j \in [1, N]\). We want to emphasize here, that this definition of hybridization depends on the order (index) of the states. Therefore, it is necessary to scan the spectrum for energy level crossings before interpreting the results.

3. State Activity

We are particularly interested in the optical properties of the hybrid system and the modifications thereof as we increase the coupling strength and change the position of the adatom. Therefore, it is not only necessary to identify the configurations which modify the electronic states in general, but in particular we aim to modify the set of states that is optically active, i.e., that is responsible for the optical properties. To quantify if and to what extent a state is involved in the optical interaction, i.e., how strongly it contributes to the optical absorption cross section of the system, we define the state activity \(a_{\langle j \rangle}\) of state \(|j\rangle\) as

\[
a_{\langle j \rangle} = \sum_{j' = 1}^{N} |s_{jj'}|, \tag{7}
\]

where \(s_{jj'} = |E_f - E_i|/|\langle f | \hat{r} | i \rangle|^2\) is the oscillator strength of the electronic single-particle transition \(|i\rangle \rightarrow |f\rangle\) with the real-space position operator \(\hat{r}\) acting as \(\langle l' | \hat{r} | l \rangle = \mathbf{r}_l \delta_{ll'}\). In case \(a_{\langle j \rangle} \approx 0\), we call \(|j\rangle\) optically inert. For non-degenerate states, this is equivalent to vanishing transition dipole moments between state \(|j\rangle\) and all other states \(|j'\rangle\), for example for symmetry reasons. High state activities, on the other hand, identify the given state as a donor or acceptor state for single-particle transitions in the hybrid system.

C. Optical Properties

As the central figure of merit to characterize the optical properties of the system we choose the linear absorption cross section \(\sigma_{\text{abs}}(\omega)\). All measures mentioned above are quantizers that characterize single-particle energy states. So far, we have not been asking if these states are actually occupied by electrons or not. This is, however, crucial to determine the absorption cross section, which makes it a property not only of the energy level diagram itself, but also of the number of electrons that populate it. Throughout the whole paper, we assume half filling of the energy landscape, corresponding to one mobile electron per atomic site orbital. Consequently, all states below the Fermi energy are occupied by two electrons and are unoccupied above. To isolate the interaction-mediated effects from the characteristics of the optical response
FIG. 1. Jablonski energy level diagrams (bottom left panel) and real-space illustrations of single-particle states (bottom right panel) of (a) the linear chain, (b) the dimer chain, and (c) the topological insulator composed of \( N_a = 70 \) atoms. The chains are illustrated in the top panel, where solid dark lines between neighboring atoms represent strong bonds and dashed light lines represent weak bonds. The black diamonds and color of the circles in the bottom right panels represent the real-valued expansion coefficients \( c_{jl} \) of the states \( |j\rangle \), whereas the size of the colored circles encodes their squared absolute values \( |c_{jl}|^2 \).

We show the two single-particle states that are lowest and highest in energy, \( j \in \{1, 2\} \) and \( j \in \{69, 70\} \), respectively. They are qualitatively equivalent for all three structures. Moreover, we depict representatives of the states that are most relevant for the optical interaction of the structure. They are located around the particle-hole symmetry line at \( E = 0 \), which is also the Fermi energy for half filling. The topological insulator exhibits two strongly localized (nearly) degenerate edge states inside the band gap close to \( E = 0 \).

that rely on the single-particle energy level diagram, we distinguish between the non-interacting and the interacting absorption cross sections, \( \sigma_{\text{abs}}^{\text{ni}}(\omega) \) and \( \sigma_{\text{abs}}^{\text{i}}(\omega) \). The latter includes Coulomb interaction between electrons in the system, whereas the former does not.

The non-interacting absorption cross section of the hybrid system can be expressed as

\[
\sigma_{\text{abs}}^{\text{ni}}(\omega) \propto \sum_{i < f} \delta_\varepsilon (E_f - E_i - \hbar \omega),
\]

where \( s_{if} \) is again the oscillator strength and \( \delta_\varepsilon \) denotes Dirac’s delta distribution broadened to a Lorentzian by a parameter \( \varepsilon = 20 \text{ meV} \) according to \( \delta_\varepsilon(x) = 2\varepsilon/(x^2 + \varepsilon^2) \).

The indices \( i \in [1, \text{HOMO}] \) and \( f \in [\text{LUMO}, N] \) denote the set of occupied initial single-particle states from below the Fermi energy and unoccupied final single-particle states from above the Fermi energy of the non-interacting system, respectively, that contribute to the transition \( |i\rangle \rightarrow |f\rangle \).

To compute the interacting absorption cross section \( \sigma_{\text{abs}}^{\text{i}}(\omega) \), we probe the system with a small-amplitude spectrally broad electric field pulse \( \mathbf{E}(t) = E(t)\hat{e}_x \), polarized along the chain direction \( (x) \), and record the resulting dipole moment \( \mathbf{p}(t) \). The system’s response to a pulse polarized perpendicular to the chain direction is much smaller and at much higher energy and, therefore, neglected in this work. The way we take into account the induced Coulomb interactions and details on the computation of \( \mathbf{p}(t) \) can be found in App. A.

After Fourier transforming both quantities, we calculate the frequency-dependent polarizabilities according to \( \alpha_{x,x}(\omega) = p_x(\omega)/E_x(\omega) \) and \( \alpha_{x,y}(\omega) = p_y(\omega)/E_x(\omega) \). We then obtain the interacting absorption cross sections as

\[
\sigma_{x,y,\text{abs}}^{\text{i}}(\omega) \propto \omega \text{Im}[\alpha_{x,x,\text{abs}}(\omega)],
\]

and \( \sigma_{\text{abs}}(\omega) = \sigma_{x,\text{abs}}(\omega) + \sigma_{y,\text{abs}}(\omega) \), where \( \text{Im}[\cdot] \) denotes the imaginary part. In Eq. (9), the Coulomb part is scaled by the parameter \( \lambda \) that (numerically) controls the Coulomb interaction strength. Setting \( \lambda \rightarrow 0 \) retrieves the non-interacting absorption cross section in Eq. (8) (see details in App. A).

III. DISCUSSION AND RESULTS

In the following, we successively discuss the electronic and optical properties of the stand-alone SSH chains, the hybrid chain-adatom system without Coulomb interaction, and finally the interacting hybrid chain-adatom system.
FIG. 2. Non-interacting absorption spectrum $\sigma_{\text{abs}}^{\text{ni}}(\omega)$ for the linear chain (green dotted line), the dimer chain (brown solid line), and the topological insulator (yellow dashed line) for the parameter set given in Sec. II A assuming half filling of the energy level diagram. The data of the linear chain have been scaled with the factor 1/4 to match the order of magnitude of the other two structures.

A. Stand-Alone 1D SSH Chains

As a first application, we study the three 1D molecular chains of the SSH model: the linear chain, the dimerized chain, and the topologically insulating chain. To create a topologically non-trivial system, we choose the number of atoms $N_a$ in our system to be even. The Hamiltonian reads

$$\mathcal{H}_{\text{TB}}^{\text{chains}} = - (t - \Delta) \sum_{\text{even } l=2}^{N_a-2} \left( |l\rangle\langle l + 1| + |l + 1\rangle\langle l| \right) - (t + \Delta) \sum_{\text{odd } l=1}^{N_a-1} \left( |l\rangle\langle l + 1| + |l + 1\rangle\langle l| \right),$$

where we use the hopping parameter value of bulk graphene $t = t_{ll'} = 2.66 \text{ eV}$ and $\Delta = 0$ for the linear chain, $\Delta = 0.3t$ for the dimer chain, and $\Delta = -0.3t$ for the topological insulator. The transition from the semiconducting or insulating topologically trivial dimer chain ($\Delta > 0$) to the non-trivial topological insulator ($\Delta < 0$) takes place by crossing $\Delta = 0$ via the gap-less linear chain. As $\Delta$ approaches zero from above, the dimer chain’s band gap decreases, it closes for $\Delta = 0$ (linear chain), and opens up again for negative $\Delta$, however, bringing forth the two near-zero edge states of the topological insulator.

Figure 1 shows the energy level diagrams and several selected characteristic single-particle states of (a) the linear chain, (b) the dimer chain, and (c) the topological insulator made up by $N_a = 70$ atoms. As mentioned above, we assume half filling of the energy landscape, such that all states below (above) the Fermi energy $E = 0$ are doubly occupied (unoccupied) in the linear chain and the dimer chain. The topological insulator exhibits two nearly degenerate edge states close to the Fermi energy $E = 0$ that we populate with one electron each. We immediately notice that both the low-energy and the high-energy states are conceptually equivalent for all three structures. The physical difference between the systems becomes more pronounced the closer one gets to the energetic region around the Fermi energy $E = 0$. However, this is also the energetic region where we find the single-particle states that are predominantly active in the optical interaction of the investigated systems. Therefore, we can indeed expect substantially differing optical responses from the three structures as we will show in the following.

1. Linear Chain

The discrete energy level diagram of the finite linear chain in Fig. 1 results from quantizing the metallic band structure of the infinite chain. Additionally to the above mentioned low- and high-energy states, we show the HOMO and LUMO states. Their structures can be described as two nested modes of quarter wavelength shape of even and odd symmetry, respectively, on the two sublattices of the chain. In Fig. 2 the green dotted line shows the linear chain’s non-interacting absorption cross section as a function of the excitation energy. The energy of the most prominent low-energy absorption mode around $\hbar\omega = 0.24 \text{ eV}$ coincides exactly with the energy difference of the HOMO and LUMO states.
To confirm the obvious conclusion, we quantify the contributions of single-particle transitions in the linear chain to the absorption spectrum with the state activity \( a_{ij} \). Figure 3a (green diamonds) shows the state activity of all single-particle states of the linear chain. Indeed, we note that the HOMO and LUMO are the only states that significantly contribute to the non-interacting absorption spectrum. It can, therefore, be concluded that the prominent low-energy mode at \( \hbar \omega = 0.24 \text{ eV} \) corresponds to the electronic transition \( |\text{HOMO}\rangle \rightarrow |\text{LUMO}\rangle \). Furthermore, we note, that besides the states HOMO−2, HOMO−1, LUMO+1, and LUMO+2, all other single-particle states are optically inert, i.e., \( a_{ij} \approx 0 \). This is in stark contrast to the activity of the single-particle states of the dimer chain and the topological insulator, as can be seen from Fig. 3b, as well (brown squares and yellow circles). To engineer the optical properties of the linear chain, it is, therefore, desirable to either modify the optically active HOMO and LUMO states or to increase the optical activity of other states that are located further away from the Fermi energy by means of coupling the adatom to the system.

Figures 3c–d show the localizations \( L_{ij} \) of the three chains’ states. It is interesting to notice that the localization of all the linear chain’s states have the exact same value and do not fall below a critical localization \( L_{\text{crit}} \). We can compute this value by plugging the analytical solution of the SSH model \( \psi_{1l} \) for the linear chain’s lowest-energy state \( c_{1l} = \sqrt{2/N_a+1} \sin \left( \frac{\pi l}{N_a+1} \right) \), for instance, into Eqs. (3) and (4). We obtain \( L_{\text{chain}}^{(1)} = \frac{1}{3} \left( 1 - \frac{1}{N_a-1} \right) \), which evaluates to 0.33 for a chain of length \( N_a = 70 \). It can further be shown, that all single-particle states of the linear chain evaluate to this exact same value, \( L_{ij} = L_{\text{crit}} \) independent of \( j \).

### 2. Dimer Chain

The energy level diagram of the dimer chain in Fig. 1b is of insulating character. We observe a lower-lying and a higher-lying quasi-continuum of states which would constitute the valence band and the conduction band in the limit of an infinitely extended chain \( (N_a \rightarrow \infty) \), with a band gap of size \( 4|\Delta| \approx 3.19 \text{ eV} \). Besides the low- and high-energy states, Fig. 1b also shows the HOMO and LUMO states of the dimer chain. They display two nested modes of half wavelength shape of even and odd symmetry, respectively. We notice that especially the states around the Fermi energy exhibit a dimerized nature, i.e., neighboring atoms act alike and behave collectively as a two-atomic unit cell and not as individual atoms anymore. This is not the case for the low- and high-energy modes that conceptually look similar to the corresponding modes of the linear chain. Just as for the linear chain, the single-particle transition from HOMO to LUMO produces the most prominent resonance at 3.19 eV at the lower edge of the quasi-continuum in Fig. 2 (brown solid line). Unlike in the case of the linear chain, however, the absorption spectrum is much richer. We observe many more modes above 3.19 eV that are of the same order of magnitude as the most prominent one. A way to consistently complement this finding is through the state activities of the dimer chain in Fig. 3b (brown squares). Although the HOMO and LUMO states exhibit the highest state activity here as well, many states around \( E = 0 \) are optically active and contribute to the absorption spectrum, and none of them is completely inert. As a consequence, many pairs of optically active states couple and lead to the formation of the quasi-continuum of comparatively dense lying absorption modes above the band gap.

The slightly different localization values for the dimer chain’s and topological insulator’s states \( j = 18 \approx N_a/4 \) and \( 53 \approx 3N_a/4 \) with respect to other states in Figs. 3c–d do not affect the optical properties of the structure substantially due to the low activity of these states.

### 3. Topological Insulator

The energy level diagram of the topological insulator in Fig. 1c strongly resembles the one of the dimer chain and is of insulating character as well. The states \( j = 34 \) and \( j = 37 \) are conceptually equivalent to the HOMO and LUMO of the dimer chain. However, we additionally find two near-zero degenerate states inside the band gap. They are strongly localized at the edges of the chain and attain localization values close to 1, as is shown in Fig. 3a. Moreover, Fig. 2a reveals that they are mildly optically active as well, which leads to the formation of a few absorption peaks in Fig. 2 (yellow dashed line) on the outskirts of the quasi-continuum in the range between \( \hbar \omega = 2|\Delta| \) and \( \hbar \omega = 4|\Delta| \). This distinguishes the absorption spectrum of the topological insulator from the one of the dimer chain of equal length. While the most prominent mode at 3.19 eV is present in both insulating systems, the spectral position of the modes differ more the higher the energies of the modes get. The highest energy modes of the dimer chain and topological insulator, presented in Fig. 2 show this complementary behavior.

### B. Hybrid Chain-Adatom System

In the previous sections, we have discussed the electronic and optical properties of the stand-alone chain antennas. In the following, we will discuss the optical absorption in the presence of an adatom when \( t_e = t_g > 0 \). It is instructive to first investigate the case of non-interacting electrons. Within this idealized model one may directly deduce how modifications, that the single-particle states undergo upon sensing the adatom’s presence and that are due to the hybridization with the newly introduced adatom states, translate into optical properties through Eq. (8). In contrast, effects that manifest
due to Coulomb interaction can be analyzed in an isolated manner from the previously mentioned aspect and are discussed in Sec. III C.

Figure 1 shows the non-interacting absorption cross section of the hybrid chain-adatom systems as a function of coupling strengths, i.e., varying chain-adatom distances or TLS dipole orientations, and for different chain coupling atoms $l_c$. The evolution of the system as a function of the chain-adatom coupling strength is presented in Figs. 5 and 6. The former shows the state activity, the hybridization measure, and the localization of those states of the hybrid linear chain-adatom system that are close to the Fermi energy. The latter depicts the energy landscape of the three chains as a function of chain-adatom coupling strength; the color of the lines encodes the parity of the wavefunction part on the chain of the respective states according to $P(j) = \langle j|\hat{P}|j\rangle = \sum_{l=1}^{N_A} c_j^* c_{j+l}$. In general, we note the linear chain to be much more prone to hybridize with the adatom and change its optical properties than the other systems under consideration. We show the main results for all three SSH model structures. However, we limit our detailed discussion to the more attractive case of the linear chain.

1. Coupling to the Edge

The absorption spectra of the hybrid linear chain-adatom system in the top row of Fig. 4 show that the coupling position plays a crucial role for the optical absorption. While coupling to $l_c = 1$ and $l_c = 3$ shows a similar effect, we notice that the absorption spectrum of the system is barely affected if one couples the adatom to $l_c = 2$. This observation can be explained via the absolute value of the real-space expansion coefficients $|c_{j1}|$ and $|c_{j2}|$ of the stand-alone chain’s energy eigenstates, which are energetically closest to the adatom’s states at $\pm 0.5$ eV. They are significantly larger than $|c_{j2}|$. In fact, $|c_{j2}| \approx 0$ holds true not only for the HOMO and LUMO states (as can be seen in Fig. 1b), but also for the other states in the vicinity of the Fermi energy $E = 0$. As a consequence, coupling effects are negligible in this configuration.

In Figs. 4a and 5, we notice a strong red-shift of the most prominent low-energy HOMO-LUMO transition mode which is accompanied by a decrease in energy difference of the HOMO and LUMO states in the energy landscape, as can be confirmed in Fig. 6. At the same time, the mode intensity drops for higher coupling strengths, since the HOMO and LUMO states, that were of purely odd and even parity in the uncoupled case, $P = -1$ and $P = 1$, change their symmetry behavior and couple less strongly. Moreover, another prominent mode builds up in the same spectral region. As can be seen from Fig. 5, especially the states HOMO–1 and LUMO+1 become optically active, when the adatom is coupled stronger to the linear chain. Indeed, a thorough analysis of this newly occurring mode reveals that it is related to the transitions HOMO–1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+1. In Fig. 6, we see that the transition HOMO–1 $\rightarrow$ LUMO is symmetry-forbidden in the uncoupled system, since both states are of even parity $P = 1$. By increasing the coupling strength, however, the transition becomes allowed and manifests itself in Fig. 4 as the previously mentioned mode of increasing intensity.

To further illustrate the inertia of the chain to couple to the adatom for $l_c = 2$ in Fig. 4, we compare the hybridization in Fig. 3 for $l_c = 1, 3$ and $l_c = 2$. In the former two cases ($l_c = 1, 3$) we observe that all states in the given range show non-zero hybridization already for adatom coupling strength below $t$, i.e., they sense the presence of the adatom and are modified accordingly. In Fig. 3a, this is reflected in the fact that all states are spectrally shifted and lose their well-defined symmetry. In the latter case ($l_c = 2$), however, we observe a vanishing hybridization for almost all states. Please note that the hybridization values for the two states below the HOMO and above the LUMO are non-zero only be-
FIG. 5. (a) State activity $a_{ij}$ for states closely below and above the Fermi energy of the linear chain as a function of the coupling strengths $t_e = t_g$ of the adatom states to $l_c$. We investigate different coupling positions $l_c \in \{1, 2, 3, 18, 35\}$. (b) Hybridization $h_{ij}$ of the adatom states with the states of the linear chain for different coupling positions. (c) Localization of the states of the hybrid linear chain-adatom system.

FIG. 6. The energy landscape of the linear chain (a,d), the dimer chain (b,e), and the topological insulator (c,f) as a function of coupling strengths $t_e$ and $t_g$ for coupling locations $l_c = 1$ (a-c) and $l_c = 2$ (d-f). The color indicates the parity $P_{|j\rangle} = \langle j|P|j\rangle$ of the part of the wavefunction that is localized on the chain sites, and which is the discretized analogon of $\langle \psi_j(r)|\psi_j(-r)\rangle$ in our framework. The edge states of the topological insulator have been slightly shifted away from zero for the sake of better visibility.
FIG. 7. Real-space representations of the single-particle energy states of the hybrid linear chain-adatom system for different coupling strengths (a) \( t_e = t_g = 0 \), (b) \( t_e = t_g = 0.5t \), (c) \( t_e = t_g = t \), and (d) \( t_e = t_g = 2t \). The adatom is coupled to the host atom \( l_c = 18 \) in all subfigures (indicated by the black dashed line); the adatom’s states \( |e⟩ \) and \( |g⟩ \) are depicted to the left of the chain continuum. Like in Fig. 1 the circles’ color encodes the real-valued expansion coefficients \( c_{jl} \), and their size is proportional to |\( c_{jl} \)|².

2. Coupling to the Bulk

Before discussing the two right columns of Fig. 5 where we couple the adatom to bulk sites \( l_c = 18 \) and \( l_c = 35 \) of the chain, we need to understand Fig. 7 first. It shows the real-space representations of the single-particle energy states of the hybrid linear chain-adatom system for different coupling strengths \( t_e = t_g = 0 \) (a), \( t_e = t_g = 0.5t \) (b), \( t_e = t_g = t \) (c), \( t_e = t_g = 2t \) (d). We have always coupled the adatom to \( l_c = 18 \), which divides the chain geometrically according to the ratio 1:3. In the decoupled system (a), the linear chain and the adatom are not hybridized and the real-space wavefunction either lives completely on the adatom orbitals (\( |e⟩ \) and \( |g⟩ \)) or completely on the chain (all other states). When we increase the coupling (decrease the distance of the adatom to the chain or align its dipole moment suitably), we observe in Fig. 7 that we induce population on the adatom’s sites for a significant number of energy eigenstates. Simultaneously, the wavefunctions of the lowest-energy and highest-energy states get attracted by the adatom. By further increasing the coupling strength (Figs. 7c and d), we observe that the adatom acts as a potential barrier for the wavefunction and effectively splits the chain apart into two stand-alone chains of smaller lengths. The real-space wavefunctions of most of the energy eigenstates are apparently locked on either side of the chain. Exceptions thereof are i) the lowest-energy (\( j = 1 \)) and highest-energy (\( j = 72 \)) modes which are strongly localized on the adatom and in the close vicinity of the coupling atom, and ii) the
HOMO and LUMO of the strongly coupled system which are localized on the adatom and on the shorter part of the chain. It is interesting to observe that the single-particle electronic structure of the whole hybrid system seemingly collapses into a small chain on the left of the adatom in Fig. 7 and a longer part on the right. The 18 atoms belonging to the smaller sub-part of the chain host 9 prominent energy eigenstates below the Fermi energy and 9 above. This sums up to 18 states, which is exactly the expected structure for a stand-alone linear chain of 18 atoms. The larger part of the chain behaves accordingly. Especially in the vicinity of the Fermi energy where the optically active states are hosted, we notice that every fourth state is localized on the left shorter side of the system, reflecting the partitioning ratio of the chain. These geometrical features are also apparent in the localization figure of merit in Fig. 5 for $l_c = 18$, where we see that one in four states shows a substantially increased localization for high coupling strengths, when the real-space wavefunction is localized on only 18 atoms. Moreover, we notice that the adatom population on the optically active states in the region around the Fermi energy is maximum for intermediate couplings rather than for larger or smaller ones.

In the non-interacting absorption spectrum of this configuration shown in Fig. 4, this translates to the emergence of two prominent modes for high coupling strengths. We observe that the resonant mode at 0.24 eV in the un-coupled case evolves toward two modes at 0.33 eV and 0.98 eV. While the former energy coincides with the HOMO-LUMO gap of a stand-alone chain made up by 52 atoms, the latter is equivalent to the HOMO-LUMO gap of an 18-atomic chain. Equivalently, Fig. 4 shows the spectrum of the configuration where the chain is split close to the middle. Effectively, the 70-atomic chain with HOMO-LUMO gap of 0.24 eV collapses into two 35-atomic chains with HOMO-LUMO gaps of 0.49 eV, which results in the appearance of a mode at 0.49 eV for high coupling strengths. Moreover, Fig. 6 for $l_c = 35$ further reveals that besides the HOMO and LUMO states which have a significant share of population concentrated on the adatom for high coupling strengths, all other states attain a similar localization value, just as it was the case for the stand-alone linear chain. In this case, however, the wavefunctions are localized on one of the two almost equally long sides of the chain. This leads to localization values around $L_{ij} \approx 0.67$.

C. Interacting Hybrid System

So far, we have considered non-interacting electrons. In insulating electronic systems whose optical properties are predominantly characterized by single-particle transitions, Coulomb interaction may often be safely neglected [19]. However, previous contributions have revealed that especially in the metallic linear chain, Coulomb interaction leading to collective plasmonic charge carrier oscillations plays a significant role for determining resonant modes [19, 64–69]. To elucidate this, we show the absorption spectra of all three stand-alone structures in Fig. 3 as a function of the Coulomb interaction strength $\lambda$ introduced in App. A.

In Fig. 8a, we verify that the linear chain’s optical modes strongly depend on the Coulomb interaction strength in a continuous way. The lowest-energy most prominent mode shifts from $\hbar \omega = 0.24$ eV for $\lambda = 0$ (Coulomb interaction turned off) to 0.67 eV for $\lambda = 1$ (Coulomb interaction fully taken into account). The next higher mode even changes its spectral position by more than 1 eV upon turning on electron-electron interaction. We conclude that to properly find resonant modes of the combined linear chain-adatom system, performing interacting simulations which take into account Coulomb repulsion is inevitable for the hybrid system as well. However, Fig. 8a also reveals that the transition from the lowest-energy mode of the non-interacting system to the corresponding mode of the interacting system is smooth and continuous. It can therefore be concluded that the HOMO and LUMO continue to constitute the predominantly involved single-particle states in the formation of this resonance also in the interacting system. More detailed investigations concerning this issue have been performed and similar conclusions have been drawn in the context of non-interacting and interacting molecular chains in a TB framework [65], in time-dependent density functional theory [19], and upon exact diagonalization [66], as well as in metallic gold nanospheres [69, 70], and in structured...
FIG. 9. Square root of the interacting absorption cross sections \( \sqrt{\sigma_{\text{abs}}(\omega)} \) of the linear chain (a-e), the dimer chain (f-j), and the topological insulator (k-o). The very left column shows the absorption cross section in case the adatom is coupled to atom \( l_c = 1 \) of the chain. The other columns show the same quantity for other coupling positions.

The adatom to the bulk atoms (Figs. 9h and c), however, paves the way for manipulating the modes in the range between 0.35 eV and 1 eV for \( l_c = 18 \) (Fig. 9i), and between 0.35 eV and 1.5 eV for \( l_c = 35 \) (Fig. 9j). Consistent with Fig. 8b, the apparent modes are blue-shifted with respect to the non-interacting systems.

IV. SUMMARY

In this paper, we have investigated the tunability of the optical modes of one-dimensional atomic chains upon coupling them to adatom impurities. To that end, we have presented a tight-binding based hybrid system model for an atomic SSH chain, applicable to linear organic molecules such as polyenes, that is coupled to an adatom treated as a two-level system. We investigated in detail how the adatom influences the real-space representations of the model Hamiltonian’s single-particle eigenstates and how the optical absorption cross section is modified as a function of coupling strength between the adatom and the chains. We have shown that in certain coupling positions the adatom may significantly modify the optical properties especially of the metallic linear chain antenna already for comparably small coupling strengths. We conclude that at high coupling strengths, the adatom acts as a potential barrier and effectively splits the chain apart into two sub-systems. For suitable parameter sets, this is reflected as well in the absorption spectrum which no longer shows one single pronounced low-energy mode, but two higher-energy modes that stem from the states of two smaller chains. We find that the dimerized chain and the topological insulator described within the Su-Schrieffer-Heeger model remain both relatively inert to the presence of the adatom. The linear chain’s modes, however, can be readily tuned over a broad spectral region by changing the interaction strengths that couple the adatom to the chains, i.e., the distance of the adatom to the chain or the orientation of its dipole moment.

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Appendix A: Computation of the time-dependent dipole moment $p(t)$

The Hamiltonian of the hybrid system which is coupled to a time-dependent electric field $E(t)$ reads

$$H(t) = H_{\text{antenna}} + H_{\text{TLS}} + H_{\text{interaction}} - e \varphi(t), \quad (A1)$$

where the time-independent part is given by Eq. (1), $e$ is the electronic charge, and $\varphi(t) = \varphi^{\text{ext}}(t) + \varphi^{\text{ind}}(t)$ is the total electric potential, composed of the externally applied potential $\varphi^{\text{ext}}(t) = -r_{1} \cdot E(t)$ and the induced potential $\varphi^{\text{ind}}(t) = -\lambda e N_{e} \sum_{\ell} v_{\ell}^{\text{hyb}} (\rho_{\ell}(t) - \frac{1}{N})$ at orbital $\ell$. Here, $N_{e}$ is the number of electrons in the system and $v_{\ell}^{\text{hyb}}$ denotes the Coulomb interaction matrix element which couples the charges on sites $\ell$ and $\ell'$. The parameter $\lambda \in [0, 1]$ has been introduced to artificially turn on and off the Coulomb interaction in the simulations. The elements of the Coulomb matrix that couple antenna orbitals to other antenna orbitals are constructed as follows: For the onsite-values, nearest-neighbor-, and next-to-nearest-neighbor-values, we apply values calculated by Potasz et al. [22]: the values coupling sites further away from each other follow the $1/r$ Coulomb power law. We outline the construction of the adatom’s contributions to the Coulomb matrix $v_{\ell}^{\text{hyb}}$ in App. [13]. The density matrix $\rho$ is initialized as $\rho^{0} = \frac{1}{N} \sum_{j} |j\rangle \langle j|$, where $f_{j}$ is the occupation of the energy eigenstate $|j\rangle$ of the Hamiltonian given in Eq. (A1) without externally applied electric field, and the factor 2 in the numerator accounts for spin degeneracy. The density matrix is propagated through time according to the master equation

$$\frac{\partial}{\partial t} \rho(t) = -i \hbar [H(t), \rho(t)] - \frac{1}{\tau} (\rho(t) - \rho^{0}). \quad (A2)$$

Here, $\hbar^{-1} = 10 \text{ meV}$ is a phenomenological scattering energy introduced to mimic dissipation. The value is taken from doped extended bulk graphene [73]. We determine the resulting dipole moment $p(t) = \sum_{\ell} r_{\ell} q_{\ell}(t)$, where $q_{\ell}(t) = -eN_{e} \rho_{\ell}(t)$ is the charge at site $\ell$ as a function of time.

Appendix B: Computation of the inter-system values of the total Coulomb matrix $v_{\ell}^{\text{hyb}}$

The extended Coulomb interaction matrix $v_{\ell}^{\text{hyb}}$ for the hybrid system is based on the interaction matrix of the stand-alone antenna $v$. The latter is determined as described in previous contributions [41, 73]. The construction of $v_{\ell}^{\text{hyb}}$ is as follows:

$$v_{\ell \ell'}^{\text{hyb}} = \rho_{\ell \ell'}, \quad \text{for } \ell, \ell' \in [1, N_{a}], \quad (B1)$$

Like on the diagonal of $v$, we impose the on-site values $v_{\ell \ell} = 16.52 \text{ eV}$ on the part of $v_{\ell}^{\text{hyb}}$ which corresponds to the adatom sites, $v_{gg}^{\text{hyb}} = v_{ee}^{\text{hyb}} = v_{eg}^{\text{hyb}} = v_{ge}^{\text{hyb}} = v_{nn}$. The inter-system elements which couple the antenna and the adatom are determined according to

$$v_{cl}^{\text{hyb}} = v_{lc}^{\text{hyb}} = v_{l e} = \frac{\alpha_{cc}}{d + \alpha_{cc}} \sqrt{\frac{t_{e}}{t}}, \quad (B2)$$

$$v_{pl}^{\text{hyb}} = v_{lp}^{\text{hyb}} = v_{l e} = \frac{\alpha_{cc}}{d + \alpha_{cc}} \sqrt{\frac{t_{e}}{t}}, \quad (B3)$$

$$v_{cl}^{\text{hyb}} = v_{lc}^{\text{hyb}} = v_{nn} = \frac{\alpha_{cc}}{d} \sqrt{\frac{t_{e}}{t}}, \quad (B4)$$

$$v_{gl}^{\text{hyb}} = v_{lg}^{\text{hyb}} = v_{nn} = \frac{\alpha_{cc}}{d} \sqrt{\frac{t_{e}}{t}}, \quad (B5)$$

where $l \in [1, N_{a}] \backslash \{t_{c}\}$ and $v_{nn} = 8.64 \text{ eV}$ is the experimentally determined nearest-neighbor value for honeycomb carbon [72]. $d$ is the distance of the adatom to the coupling atom $t_{c}$ and $\alpha_{cc} = 1.42 \text{ Å}$ is the distance of two carbon atoms in the antenna. The distance $d$ relates to the couplings according to $t_{e, g} = t \left(\frac{\alpha_{cc}}{d}\right)^{2}$ [74] and the intra-antenna values $v_{ll}$ are determined through Eq. (B1).

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