Coulomb-Engineered Heterojunctions and Dynamical Screening in Transition Metal Dichalcogenide Monolayers

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The manipulation of two-dimensional materials via their dielectric environment offers novel opportunities to control electronic as well as optical properties and allows to imprint nanostructures in a non-invasive way. Here we assess the potential of monolayer semiconducting transition metal dichalcogenides (TMDCs) for Coulomb engineering in a material realistic and quantitative manner. We compare the response of different TMDC materials to modifications of their dielectric surrounding, analyze effects of dynamic substrate screening, i.e. frequency dependencies in the dielectric functions, and discuss inherent length scales of Coulomb-engineered heterojunctions. We find symmetric and rigid-shift-like quasi-particle band-gap modulations for both, instantaneous and dynamic substrate screening. From this we derive short-ranged self energies for an effective multi-scale modeling of Coulomb engineered heterojunctions composed of an homogeneous monolayer placed on a spatially structured substrate. For these heterojunctions, we show that band gap modulations on the length scale of a few lattice constants are possible rendering external limitations of the substrate structuring more important than internal effects. We find that all semiconducting TMDCs are similarly well suited for these external and non-invasive modifications.

I. INTRODUCTION

In (quasi) two-dimensional (2D) materials the Coulomb interaction is enhanced due to weak intrinsic screening.1–4 Modifications of the immediate surrounding via substrates, capping layers or adsorbates as depicted in Fig. 1 can therefore strongly affect the Coulomb interaction and its related effects. As a result the band gaps of 2D semiconductors are, for example, strongly influenced by the chosen substrate or capping material5–7. By embedding 2D materials in spatially inhomogeneous dielectric environments, Coulomb engineered heterostructures with spatially changing quasi-particle band gaps8–12 can be created. In recent years, this approach to non-invasively manipulate 2D materials has become a promising field of research.9,13–24

Here, we present a detailed study of Coulomb engineering effects to semiconducting transition metal dichalcogenides (TMDCs) and discuss the influence of instantaneous and frequency dependent homogeneous substrates on the band structure. Since full ab-initio GW calculations of lateral or vertical 2D heterostructures are numerically very demanding, we implement a material realistic description based on a combination of the GΔW25,26 and WFCE27 approaches. In this way we systematically investigate semiconducting TMDCs in their H-phase and present a modeling scheme to describe Coulomb-engineered heterojunctions.

For homogeneous substrates, as depicted in Fig. 1 (b), we find that the effects of instantaneous (frequency independent) dielectric functions are comparable for all materials under investigation with the transition metal sulfides slightly stronger affected. For retarded (frequency-dependent) substrate screening εsub(ω) we find symmetric shifts of the valence and conduction bands with slightly enhanced effects in the sulfides. We show that these effects from retarded dielectric functions can be approximately mapped to effective static dielectric constants. We furthermore find spatially strongly localized self-energies, which are resulting from material-intrinsic properties independently of the surrounding material. This is again very similar for all TMDCs under investigation. Based on these major findings, we can subsequently construct an efficient approach to realistically describe Coulomb-induced heterojunctions as depicted in Fig. 1 (c).
The paper is structured as follows: in section II, we introduce our theoretical approach. In the results section III, we discuss in detail the influence of homogeneous substrates with instantaneous (sec. III A) as well as retarded dielectric functions (sec. III B) on monolayer TMDCs. We analyze in section III C the substrate-induced single-particle contributions and in section III D the many-body Coulomb interaction effects in dielectrically engineered heterostructures is laid out and applied to the example case of WS$_2$ in section III D.

II. METHOD

The band structure of any solid-state material results from single particle contributions and is influenced by the many-body Coulomb interaction $W$. In the following we aim to understand how changes to $W$ of a monolayer TMDC induced by modifications of its dielectric environment affects its electronic quasi-particle band structure and particularly its band gap.

The screened Coulomb interaction $W$ in general non-local and frequency-dependent. For a freestanding TMDC monolayer it reads in momentum space:

$$W_{\text{TMDC}}^{(q,\omega)} = \frac{v_q}{\varepsilon_{\text{TMDC}}^{(q,\omega)}},$$

where $v_q$ is the bare Coulomb interaction, $\varepsilon_{\text{TMDC}}$ the dielectric function of the monolayer including only internal screening effects, and $q$ the in-plane momentum.

To consider external screening effects resulting from, e.g., dielectric substrates or capping layers, coating molecules or other layered materials in the environment, we introduce the environmental dielectric screening function $\varepsilon_{\text{env}}^{(q,\omega)}$, so that the fully screened Coulomb interaction can be written as:

$$W_{\text{env}}^{(q,\omega)} = \frac{v_q}{\varepsilon_{\text{env}}^{(q,\omega)}}.$$  \hspace{1cm} (2)

Here, the full dielectric function $\varepsilon_{\text{env}}^{(q,\omega)}$ includes external and internal screening effects. In order to study how different screening channels change the band structure of our TMDC monolayer, we make use of the so-called $G_{\Delta W}$ approach.

To this end, we start with an ab-initio $G_0W_0$ calculation for the free-standing monolayer utilizing the full band-structure (including a significant amount of unoccupied states) with $W_0$ corresponding to $W_{\text{TMDC}}$ as defined in Eq. (1). The resulting band structure is thus already affected by the internal screening processes of the TMDC layer itself. We subsequently down-fold this $G_0W_0$ band structure to a minimal three-band / three-orbital model using adequately chosen localized Wannier functions. The resulting quasi-particle Hamiltonian and corresponding Green’s function are called $H_{\text{TMDC}}$ and $G_{\text{TMDC}}$ in the following. The additional external screening effects described by $\varepsilon_{\text{env}}^{(q,\omega)}$ are subsequently added via

$$[G_{\text{env}}^{G_{\text{TMDC}}}^{-1}(\omega)]^{-1} = [G_{\text{TMDC}}^{-1}(\omega)]^{-1} + \Sigma_{\Delta W},$$ \hspace{1cm} (3)

with $G_{\text{TMDC}}^{G_{\text{env}}} = [\omega I - H_{\text{TMDC}}]^{-1}$ and using the self-energy $\Sigma_{\Delta W} = iG_0\Delta W$ defined by the product of the non-interacting Green function $G_0$ (corresponding to the Kohn-Sham DFT results as used in the initial $G_0W_0$ step) and

$$\Delta W^{(q,\omega)} = W_{\text{env}}^{G_{\text{TMDC}}} - W_{\text{env}}^{G_{\text{TMDC}}},$$ \hspace{1cm} (4)

which is the difference between the full Coulomb interaction (including internal and external screening) and the Coulomb interaction of the free-standing TMDC. In the orbital (Wannier) basis $\Sigma_{\Delta W}$ is defined by

$$\Sigma_{\Delta W}^{\alpha\beta}(k,\omega) = \int dq \int \frac{d\omega'}{2\pi} \langle \psi_\alpha^* (k,\omega') | W_{\text{env}}^{\lambda}(k-q) | \psi_\beta (k-q) \rangle^* \times 2 \text{Im} [\Delta W^{(q,\omega')}] | n_B(\omega') + n_F(k-q) \rangle, \hspace{1cm} (5)$$

where $\alpha/\beta$ and $\lambda$ are orbital and band indices, $E_k^\lambda$ eigenenergies, and $c_\lambda^\alpha(k)$ expansion coefficients of the eigenfunctions of the $G_0W_0$ Hamiltonian $H_{\text{TMDC}}$. We use Eq. (5) to simulate situations with general retarded environmental screening.

The TMDC internal dielectric function is only weakly frequency dependent as long as $\omega$ is small compared to the TMDC band gap. In the case of instantaneous external screening $\varepsilon_{\text{env}}^{(q,\omega)} \approx \varepsilon_{\text{env}}^{(q)}$ we can thus consider the total dielectric function $\varepsilon_{\text{env}}^{(q)}$ to be frequency independent as well. This allows us to use the static Coulomb-hole plus screened-exchange approximation for the self-energy which reads in the orbital basis:

$$\Sigma_{\Delta W}^{\alpha\beta}(k) =$$

\begin{align*}
&- \int \frac{d^2q}{(2\pi)^2} \sum_\lambda \Delta W^{\alpha\beta}(q,\omega = 0) c_\alpha^\lambda(k-q) c_\beta^\lambda(k-q)^* \\
&+ \frac{1}{2} \int \frac{d^2q}{(2\pi)^2} \sum_\lambda \Delta W^{\alpha\beta}(q,\omega = 0) c_\alpha^\lambda(k-q) c_\beta^\lambda(k-q)^*,
\end{align*}

where $c_\lambda^\alpha(k)$ are the coefficients of the DFT Hamiltonian in the orbital basis. The first so-called screened-exchange term affects occupied states only and shifts all valence band states in energy. The second so-called Coulomb-hole term affects both, valence and conduction bands. As a result of the interplay between these two terms, the band-gap of our monolayers is reduced for negative $\Delta W$ and enhanced for positive $\Delta W$. Since the environmental screening always decreases $W_{\text{env}}^{G_{\text{TMDC}}}(q,\omega)$ in comparison to $W_{\text{env}}^{G_{\text{TMDC}}}(q,\omega)$, $\Delta W$ is always negative, so that any surrounding material will reduce the band gap.

In the static approximation Eq. (3) allows us to define the Hamiltonian of the monolayer including the substrate
screening effects according to $H_{\text{TMDC}}(k) = H_{\text{TMDC}}(k) + \Sigma_{G\Delta W}(k)$. The diagonalization of this Hamiltonian correspondingly yields the band structure of the monolayer as function of the environmental screening $\varepsilon_{\text{env}}$. Spin-orbit coupling (SOC) can additionally be considered by a Russel-Saunders coupling with a $k$-dependent coupling parameter as described in Ref. [33]. The coupling parameters are chosen such that the SOC splittings at the valence- and conduction bands at high symmetry points match results of GGA calculations.

We get $W_{\text{TMDC}}(q, \omega = 0)$ in the orbital basis by projecting $W_0$ from our full $G_0W_0$ calculations in the Kohn-Sham basis to three Wannier orbitals, which are also used to represent $H_{\text{TMDC}}$. Afterwards, we calculate $W_{\text{env}}^{\text{TMDC}}$ using our WFCE approach. This allows us to represent the full dielectric function $\varepsilon_{\text{env}}^{\text{TMDC}}(q, \omega) = \varepsilon_{\text{TMDC}}[q, \omega, \varepsilon_{\text{env}}(q, \omega)]$ as an augmented TMDC dielectric function $\varepsilon_{\text{TMDC}}[q, \omega, \varepsilon_{\text{env}}(q, \omega)]$. Within the latter the additional environmental screening can expressed by simple dielectric constants $\varepsilon_{\text{env}}(q, \omega) = \varepsilon_{\text{env}}$ or full retarded dielectric functions $\varepsilon_{\text{env}}(q, \omega)$ as resulting from substrates or capping layers (see Appendix B for details).

![Graph](image)

**FIG. 2.** TMDC band structure modulations from substrates with instantaneous dielectric functions. (a) $G\Delta W$ band structure for WS$_2$ with $\varepsilon_{\text{sub}} = 1$ and $\varepsilon_{\text{sub}} = 10$ (without spin-orbit coupling). (b) Absolute and (c) relative differences of $G\Delta W$ band gaps (with spin-orbit coupling) compared to the band gap of freestanding TMDCs as functions of the dielectric constant $\varepsilon_{\text{sub}}$.

**III. RESULTS**

**A. Influence of instantaneous dielectric substrate screening**

We start by investigating the situation depicted in Fig. 1(b), i.e. TMDC monolayers on homogeneous dielectric substrates. In a first step, we consider instantaneous dielectric functions by setting $\varepsilon_{\text{env}}(\omega, q) = \varepsilon_{\text{sub}}(q)$, where we choose the momentum dependence such that we can assign a static and local substrate dielectric constant $\varepsilon_{\text{sub}}$ to it, which is appropriate for bulk semiconducting substrates. This changes the long-wavelength limit of the total dielectric function to $\varepsilon_{\text{env}}^{\text{TMDC}}(q \to 0) = \varepsilon_{\text{sub}}$, while the short-wavelength behavior is unaffected $\varepsilon_{\text{env}}^{\text{TMDC}}(q \to \infty) = \varepsilon_{\text{TMDC}}(q)$ (see Appendix B).

In Fig. 2(a) we show the band structure of freestanding ($\varepsilon_{\text{sub}} = 1$) WS$_2$ together with the resulting band structure for $\varepsilon_{\text{sub}} = 10$ without spin-orbit coupling in the minimal basis of the three transition d orbitals $d_{z^2}$, $d_{xy}$ and $d_{x^2-y^2}$. Upon increasing the environmental screening we decrease the Coulomb interaction and thus decrease the band gap. In more detail, we find a constant reduction of the gap between valence and conduction bands throughout the whole Brillouin zone. This “scissor-like” behavior is a direct result of the non-local screening the TMCD monolayer is exposed to and which leads to a strongly peaked $\Delta W(q)$ in momentum space as discussed for the example of WS$_2$ in detail in Ref. [22].

In the following, we concentrate on the comparison between different TMDCs and their reactions to their dielectric environments. To this end we calculate the band gaps $E_g(\varepsilon_{\text{sub}})$ (considering spin orbit coupling) for different dielectric constants for all four TMDCs and show the absolute band-gap differences $\Delta E_g(\varepsilon_{\text{sub}}) = E_g(\varepsilon_{\text{sub}}) - E_g(\varepsilon_{\text{sub}} = 1)$ as well as the relative ones $\Delta(\varepsilon_{\text{sub}}) = \frac{E_g(\varepsilon_{\text{sub}}) - E_g(\varepsilon_{\text{sub}} = 1)}{E_g(\varepsilon_{\text{sub}} = 1)}$ in Fig. 2(b) and Fig. 2(c), respectively.

We see significant band-gap reductions with increasing environmental screening for all TMDCs. For $\varepsilon_{\text{sub}} = 5$ the band gaps are reduced by about 300 to 350 meV depending on the specific material [c.f. Fig. 2(b)]. Realistic substrates, such as SiO$_2$ or Si have macroscopic dielectric constants of about 3.6 [34] and 12 [35], respectively, yielding reductions of up to 500 meV.

The sulfides are slightly stronger affected than the selenides with larger absolute changes in their band gaps. For $\varepsilon_{\text{sub}} = 5$ the sulfides are reduced by about 300 to 350 meV. As was also found by Winther and Thygesen for the comparison between MoS$_2$ and MoSe$_2$, the MSe$_2$ compounds have smaller band gaps and thus exhibit larger internal polarizabilities so that changes in the external screening affect the total screening in the selenides less than in the sulfides. However, these differences are of quantitative rather than qualitative nature.
Indeed, the relative substrate-induced band-gap reductions as shown in Fig. 2 (c) are very similar for all materials and amount to about 15% for $\varepsilon_{\text{sub}} = 5$.

**B. Frequency-dependent substrate screening**

In realistic experimental situations the screening by substrates, capping layer, or molecular adsorbates will be dynamic, i.e. the external dielectric function will be frequency dependent. Generally, phonons and (interband) plasmons contribute to this frequency dependence. While our formalism is general, we focus in the following on the effects of interband plasmons in the substrate resonance frequencies $\omega_p$ and fixed $\varepsilon_{\text{sub}}^{(0)} = 10$ together with the free-standing band structure. We see the three cases: for small $\omega_p = 0.2$ eV the conduction and valence bands are nearly unaffected, as the substrate-screened quasi-particle band structure (dashed lines) falls on top of the freestanding one (solid lines). For large $\omega_p = 10$ eV we find the strongest, symmetric renormalization as discussed in the previous parts.

In Fig. 3 we show the resulting spectral functions for WS$_2$ for different substrate resonance frequencies $\omega_p$ and fixed $\varepsilon_{\text{sub}}^{(0)} = 10$ together with the free-standing band structure. We see the three cases: for small $\omega_p = 0.2$ eV the conduction and valence bands are nearly unaffected, as the substrate-screened quasi-particle band structure (dashed lines) falls on top of the freestanding one (solid lines). For large $\omega_p = 10$ eV we find the strongest, symmetric renormalization as discussed in the previous parts.

The band gap is always symmetric about $\omega_p = 0$, which is on the order of $\omega_p$. For intermediate $\omega_p = 2$ eV, which is on the order of the monolayer band gap, we see smaller renormalizations and side bands resulting from the coupling between the TMDC electrons and bosonic substrate excitations. For the valence bands these accompanying satellite bands appear at lower frequencies (shifted by about $-\omega_p$), and for the conduction bands at higher frequencies (shifted by about $+\omega_p$).

In Fig. 4 we show the renormalization of the valence (v) and conduct (c) band edges

$$\Delta_{\text{v/c}}(\omega_p) = E_{\text{FV/c}}^{\text{FS}} - E_{\text{V/c}}^{\text{FS}}(\omega_p)$$

and the total band-gap modification $\Delta E_g(\omega_p) = \Delta_{\text{v}}(\omega_p) - \Delta_{\text{c}}(\omega_p)$ in dependence of $\omega_p$, where $E_{\text{FV/c}}^{\text{FS}}(\omega_p)$ are the renormalized quasi-particle energies at $\mathbf{K}$. We see a negative shift of the conduction band and a positive shift in the valence band, yielding a decreasing band gap with increasing $\omega_p$. The band gap is always symmetrically reduced and the screening induced changes are generally slightly bigger in the sulfides than in the selenides, as discussed for the static dielectric function above.
Based on these monotonous symmetric shifts we can define for each frequency $\omega_p$ an effective static dielectric constant $\varepsilon_{\text{eff}}(\omega_p)$ which leads to the same renormalization of the quasi-particle band structure as the frequency-dependent external dielectric function. To this end, we combine the data from Fig. 4 (c) and Fig. 2 (b). The resulting effective $\varepsilon_{\text{eff}}(\omega_p)$ is shown in Fig. 4 (d). Both limits of the plasmon-pole model can be clearly seen: in the lower limit of $\omega_p$ the substrate screening vanishes $\varepsilon_{\text{eff}}(\omega_p \to 0) \to 1$ so that the band structures are not affected, as seen in Fig. 3 (a). For large $\omega_p$, $\varepsilon_{\text{eff}}$ recovers the static dielectric constant $\varepsilon_{\text{eff}}(\omega_p) = \varepsilon_{\text{sub}}(0) = 10$. Noticeable, the effective dielectric constant $\varepsilon_{\text{eff}}(\omega_p)$ has nearly the same $\omega_p$-dependence for all four TMDCs and thus does not show any strong material dependencies.

For our further discussions of the Coulomb engineered heterostructures we can thus stick to the static limit of the $G\Delta W$ approach utilizing effective instantaneous dielectric constants $\varepsilon_{\text{eff}}$ as along as we assume that the relevant substrate plasmon frequencies entering $\varepsilon_{\text{sub}}$ are in the optical frequency range.

### C. Self-energy length scales

For Coulomb engineered heterostructures not only the band gap reduction but also the length scale on which this reduction takes place is important. As the extent of the self-energy is an intrinsic measure for how sharp an interface in a Coulomb engineered heterostructure as depicted in Fig. 1 (c) can be, we discuss this length scale for TMDC monolayers in the following.

In Fig. 5 (a) we show the self energies for all four semiconducting TMDCs and $\varepsilon_{\text{eff}} = 10$ in real space. The self energy curves are plotted along the real-space direction $\mathbf{a}_1 = [a,0]$ with $a$ being the lattice constant and for all orbital channels.

In the static Coulomb-hole plus screened-exchange approximation $\Sigma_{G\Delta W}$ can also be interpreted as the renormalization of the hopping matrix elements of the TMDC Hamiltonian due to screening effects from the environment. We find that all hopping elements are renormalized due to screening effects, i.e. intra- ($\Sigma^G_{G\Delta W}$) as well as inter-orbital ($\Sigma^\alpha\beta_{G\Delta W}$) terms. Most importantly we find not only local renormalizations $\Sigma^\alpha\alpha_{G\Delta W}(\mathbf{R} = 0)$ but especially non-local hopping terms are changed. The renormalization due to non-local inter-orbital terms change the hybridization of the system and are mainly responsible for the change of the band gap of TMDCs in dielectric environments (as was also discussed in c.f. Ref. [8]). In fact, we see that the local diagonal elements $\Sigma^\alpha\alpha_{G\Delta W}(\mathbf{R} = 0)_{\alpha\beta}$ have opposite signs (positive for $\alpha = d_{z^2}$ and negative for $\alpha = d_{xy}/d_{x^2-y^2}$), which shift $d_{z^2}$ states up in energies and $d_{xy}/d_{x^2-y^2}$ states down. The local terms alone (note that off-diagonal local, i.e. $\mathbf{R} = 0$, terms are zero) would thus enhance the band gap at $K$ upon increasing the environmental screening [12]. To realistically describe the modifications of the band structure and the band gap it is thus important to capture non-local effects. The largest contributions for all orbital combinations and TMDCs can be found within two unit cells which corresponds to a distance of roughly 6.2 Å to 6.6 Å (depending on the material). This length scale is similar for all investigated materials.

In real space, the self-energy is the direct product of the Coulomb interaction $\Delta W(\mathbf{R}, \omega)$ and the non-interacting Green’s function $G_0(\mathbf{R}, \omega)$

$$\Sigma_{G\Delta W}(\mathbf{R}, \omega) = i \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} e^{i\omega'\omega} G_0(\mathbf{R}, \omega + \omega') \Delta W(\mathbf{R}, \omega).$$
As $\Delta W$ is a strongly peaked function in momentum space around $q = 0$, it is nearly constant in real space as can be seen in Fig. 5 (c). Hence, the decrease of the self-energy must result from properties of the Green’s function. In Fig. 5 (b) we show $G_{0}^{\alpha\beta}(\mathbf{R}, \tau = 0^+) = \langle c_{\alpha\beta}^{\dagger} c_{\alpha\beta} \rangle$. The overall curve characteristic resembles the self-energy and shows the same length scale. Thus the spatial extent of the self-energy is determined by the spatial extent of $G_{0}$ which turns out to be the decisive material specific property to determine the intrinsic length scale of a Coulomb engineered heterostructure. As the semiconducting TMDCs under consideration have similar electronic band structures, they consequently have similar extents of $G_{0}$ which explains the similar length scales of the self-energies. Thus, Coulomb engineered heterostructures should allow for spatial band gap variations within a few lattice constants$^8$ in all semiconducting TMDCs.

D. Coulomb engineered heterostructures

![Coulomb engineered heterostructure](image)

**FIG. 6.** Top: Model for Coulomb-engineered heterostructure using a spatially structured substrate with dielectric constants $\varepsilon_1$ and $\varepsilon_2$. Bottom: Local density of states for a Coulomb-engineered heterostructure using WS$_2$ with $\varepsilon_1 = 1$, $\varepsilon_2 = 10$ and $\varepsilon_3 = 1$.

In the following we aim to describe Coulomb engineered heterostructures from spatially structured substrates as shown in Fig. 1 (c). Describing such systems is numerically very challenging due to the broken translational symmetry perpendicular to the interface of the substrate. However, as we showed above, the self-energy $\Sigma_{G\Delta W}$ is short ranged and we can use a static dielectric constant $\varepsilon_{\text{eff}}$ for the description of the substrate screening effects to the hopping matrix elements of the TMDC. We thus model the self-energy of a Coulomb engineered heterostructure with the help of the self-energies from homogeneous calculations:

$$\Sigma_{\alpha\beta}^{\text{het}}(\mathbf{R}) = \begin{cases} \Sigma_{\alpha\beta}^{\xi_1} & \text{hopping in } \xi_1 \\ \Sigma_{\alpha\beta}^{\xi_2} & \text{hopping in } \xi_2 \\ \frac{1}{2}(\Sigma_{\alpha\beta}^{\xi_1} + \Sigma_{\alpha\beta}^{\xi_2}) & \text{hopping between } \xi_i \end{cases}$$

mimicking an abrupt change of the substrate underneath. Here $\Sigma_{\alpha\beta}^{\xi_i}$ is calculated from Eq. (6) and Fourier transformed to real space. With that we get the Hamiltonian for the full heterostructure:

$$H_{\alpha\beta}^{\text{het}}(\mathbf{R}) = H_{\alpha\beta}^{\text{FS}}(\mathbf{R}) + \Sigma_{\alpha\beta}^{\text{het}}(\mathbf{R}).$$

The resulting local density of states (LDOS) for WS$_2$ on a substrate with two dielectric interfaces ($\varepsilon_{1/3} = 1$ and $\varepsilon_2 = 10$) is shown in Fig. 6. Darker red areas depict high density of states whereas the light red area corresponds to nearly zero LDOS indicating the gapped region around $E = 0$. The band gap modulation in the different areas is clearly visible and we see a symmetric band alignment, as already described in Fig. 2 (a). The change of the band gap from one region to the other is limited to a few unit cells as expected from the spatial extent of the self-energy. These results are different to our previous model calculation presented in Ref. [8], where we used the Hartree-Fock approximation which effectively neglects the Coulomb-hole part of the Coulomb-hole plus screened-exchange self-energy used here. Thus, our previous calculations showed changes to the valence band only. Taking the full self-energy into account we hence find a spatial band gap modulation reminiscent of type-I heterojunctions. In the depicted case with two dielectric interfaces we can even imprint a quantum-wire-like structure to the active TMDC layer.

IV. CONCLUSIONS

Based on a combination of the $G\Delta W$ and WFCE approaches we were able to develop a material-realistic description of Coulomb-engineered heterojunctions in semiconducting TMDC monolayers. We found that all investigated TMDCs are similarly susceptible to screening-induced band-gap reductions, which can be on the order of several hundred meV. Retardation effects in the environmental screening as expressed by the frequency dependence affect the magnitude of the band gap renormalizations in such a way, that dielectric environments with high plasmon frequencies turn out to be most effective for external band structure manipulations. The electronic quasi-particle band structures in presence of frequency-dependent external dielectrics can be described in terms of effective instantaneous dielectric functions. From an analysis of the self-energy in real-space we showed, that the spatial extension of the self-energy is a material-intrinsic property. In the case of semiconducting TMDCs this spatial extent is limited to neighboring unit cells. This localization together with the effective handling of
retarded environmental screening effects, allowed us to
derive a tight-binding based modeling scheme to describe
Coulomb-engineered heterojunctions resulting from di-
electric interfaces in the substrate. Based on these
material-realistic simulations we found that spatial band-
gap modulations reminiscent of type-I heterojunctions
can be externally and non-invasively induced in a mono-
layer of WS$_2$. This renders TMDCs promising candidates
for future applications based on Coulomb engineering.

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Appendix A: Calculation details for homogeneous
monolayer TMDCs

All ab-initio calculations were performed within the
Vienna ab initio simulation package (VASP)$^{45,46}$.
The DFT calculations were carried out within the GGA
approximation$^{47}$ utilizing a PBE plane wave basis set
with a cutoff energy of 350 eV. All structures were relaxed
on $18 \times 18 \times 1$ k-meshes until the total free energy change
was smaller than $10^{-3}$ eV. The resulting parameters are
listed in Tab. I. $G_0 W_0$ calculations were performed on a
$24 \times 24 \times 1$ k-meshes, using 280 bands, $\omega$ grids with 200
grid points within VASP default $\omega$ limits. $G_0 W_0$ cutoff
energies of 150 eV, and interlayer distances of 20 Å yielding
a good compromise between numerical feasibility and
accuracy. Due to the applied super-cell approach, the
$G_0 W_0$ results are affected by artificial self-interactions
between periodic images of the 2D layer, which yields
underestimated band gaps (see Tab. I) in comparison to
the fully converged results$^{27}$. We keep focus on band
gap changes only, which are essentially converged in the
computational setup chosen here (see Appendix D).

The freestanding Hamiltonian $H_{\text{TMDC}}$ is described in a
Wannier basis by projecting the $G_0 W_0$ results to $d_2^z$, $d_{xy}$,
and $d_{x^2-y^2}$ orbitals using the Wannier90$^{49}$ code. Appropriate
inner energy windows are chosen to include the highest
valence band and as much of the lowest conduction
bands as possible. We do not perform any maximal
localization and use only the disentanglement procedure
to maintain the dominant orbital characters.

The spin orbit coupling was considered afterwards by a
Russel Saunders coupling$^{33}$ with a $k$-dependent coupling
parameter

$$\lambda(k) = \lambda_0 \cdot e \cdot \left(1 - \frac{|k-K|}{|K|}\right)^2 \cdot e^{-\left(1 - \frac{|k-K|}{|K|}\right)^2} \quad (A1)$$

which was chosen such that spin dependent GGA band
structures are reproduced. The parameter $\lambda_0$ is equal to
the spin splitting $\Delta_{\text{SOC}}$ at the $K$ point of the GGA band
structures and is listed in Tab. I.

Appendix B: Modeling the Coulomb interaction:
Method and Parameter

We utilize our WFCE approach$^{27}$ to (A) analytically
describe all involved Coulomb interaction matrix elements $W^{\alpha\beta}$ in the orbital basis and (B) to include the
external dielectric screening effects. To this end, we fit the
density-density matrix elements of the bare Coulomb in-
teraction $v^{\alpha\beta}(q)$ and the dielectric function $\varepsilon^{\alpha\beta}(q, \omega = 0)$
of the freestanding monolayers calculated from first prin-
ciples in RPA (using a recent VASP implementation by
Kaltak$^{44}$) to analytic functions as described in Ref. $[52]$.
We start with diagonalizing the bare interaction $v(q)$

$$v_{\text{diag}}(q) = \sum_{i=1}^{3} \frac{3}{2} v_1(q) |\epsilon_i\rangle \langle \epsilon_i|, \quad (B1)$$

where $v_1(q) = \langle \epsilon_1 | v(q) | \epsilon_1 \rangle$ is the leading (i.e., largest)
eigenvalue and $\epsilon_i$ are the eigenvectors of $v(q)$ in the long-
wavelength limit $q \to 0$:

$$e_1 = \left( \begin{array}{c} 1/\sqrt{3} \\ 1/\sqrt{3} \\ 1/\sqrt{3} \end{array} \right), \quad e_2 = \left( \begin{array}{c} +4/\sqrt{6} \\ -1/\sqrt{6} \\ -1/\sqrt{6} \end{array} \right), \quad e_3 = \left( \begin{array}{c} 0 \\ +1/\sqrt{2} \\ -1/\sqrt{2} \end{array} \right). \quad (B2)$$

The leading eigenvalue can be interpreted as long wave-
length charge-density modulations to which screening ef-
fects due to environments are supposed to be strongest.
For this limit, a macroscopic treatment within contin-
umum medium electrostatics is possible. We can thus con-
nect the leading eigenvalue to macroscopic properties$^{27}$.
The other eigenvalues $v_{2/3}$ are assumed to be constant$^{52}$
and obtained by averaging over the ab-initio values. The
macroscopic eigenvalue is fitted with

$$v_1(q) = \frac{3e^2}{2}\frac{1}{2a_0 A q(1+\gamma q)}, \quad (B3)$$

where we use the area of the 2D hexagonal unit cell
$A = \frac{\sqrt{3}}{2}a^2$ and the form factor $\gamma$ which describes how
the effective height of the orbitals influences short wave-
lengths.

The screened Coulomb matrix $W(q)$ is assumed to have the same eigenbasis as $v(q)$ so that we can define its
eigenvalues via the eigenvalues of the bare interaction and the dielectric function:

$$W_i(q) = v_i(q)/\varepsilon_i(q). \quad (B4)$$

The (leading) macroscopic eigenvalue of the dielectric
function is given by$^{27,53}$

$$\varepsilon_1(q, \omega) = \varepsilon_{\infty} \frac{1 - \beta_1 \beta_2 e^{-2qd}}{1 + (\beta_1 + \beta_2) e^{-qd} + \beta_1 \beta_2 e^{-2qd}}. \quad (B5)$$
In Section IIIA we use a dielectric constant determined from the valence band splitting at \( K \) in GGA calculations.

\[
\beta_i = \frac{\varepsilon_{\infty} - \varepsilon_{\text{env},i}(\mathbf{q}, \omega)}{\varepsilon_{\infty} + \varepsilon_{\text{env},i}(\mathbf{q}, \omega)},
\]

which includes the dielectric functions of the material above and beneath the monolayer \( \varepsilon_{\text{env},i}(\mathbf{q}, \omega) \). The microscopic screening effects described by \( \varepsilon_{2/3} \) are again assumed to be momentum independent, i.e., local, constants. Thus, by fitting all \( \varepsilon_i \) to the ab initio values for the free-standing monolayers (setting \( \varepsilon_{\text{env},i}(\mathbf{q}, \omega) = 1 \)) we gain fully analytic and material-realistic models for the Coulomb interaction matrix elements \( W_{\text{TMDC}} \) in the orbital basis. The corresponding fitting parameters are given in Tab. I.

By modifying \( \varepsilon_{\text{env},i}(\mathbf{q}, \omega) \) we can additionally include external screening effects from some material below or above the monolayer yielding analytic descriptions of \( W_{\text{TMDC}} \). In the main text we consider a single substrate, i.e., we set \( \varepsilon_{\text{env},1}(\mathbf{q}, \omega) = \varepsilon_{\text{sub}}(\mathbf{q}, \omega) \) and \( \varepsilon_{\text{env},2}(\mathbf{q}, \omega) = 1 \).

Section IIIA we use a dielectric constant \( \varepsilon_{\text{sub}}(\mathbf{q}, \omega) = \varepsilon_{\text{sub}} \) and in Section IIIB we incorporate the frequency dependence via the plasmon-pole approximation and set \( \varepsilon_{\text{sub}}(\mathbf{q}, \omega) = \varepsilon_{\text{sub}}(\omega) \) according to Eq. (7).

Additionally, the WFCE approach allows us to correct the artificially introduced self-interaction effects within the super-cell setup used in the ab initio calculations. To do so, we performed RPA calculations for freestanding monolayer for different vacuum heights \( h_{\text{vac}} \) between 15 Å and 40 Å and extrapolated the results to infinite vacuum heights

\[
W_{\alpha\beta}(\mathbf{q}, h_{\text{vac}}) = W_{\alpha\beta}(\mathbf{q}, \infty) + \frac{b_{\alpha\beta}(\mathbf{q})}{h_{\text{vac}}}. \tag{B7}
\]

The fitting parameter listed in Tab. I results from fits to these extrapolated Coulomb interaction matrix elements.

### Appendix C: Substrate dielectric constants

We present macroscopic dielectric constants for a few typical substrate materials in Table II.

| Substrate | SiO$_2$ | HfO$_2$ | Si | GaAs | hBN |
|-----------|---------|---------|----|------|-----|
| \( \varepsilon_{\infty} \) | \( \approx \) 3.6 | \( \approx \) 25 | \( \approx \) 12 | \( \approx \) 13 | \( \approx \) (1.8 - 3.3) |
| Reference | [34] | [34] | [35] | [35] | [54 and 55] |

### Appendix D: G\( \Delta W \) convergence

In Fig. 7 (a) we show the WS$_2$ band gap for a substrate dielectric constant of \( \varepsilon_{\text{sub}} = 100 \) as a function of the k-grid as obtained from the \( G\Delta W \) approach. Due to the strongly peaked form of \( \Delta W(\mathbf{q}) \) in momentum space, rather fine k-meshes are needed to converge these \( G\Delta W \) calculations. We use for all static calculations \( 400 \times 400 \) k-points resulting in band gap inaccuracies smaller than 0.02 eV. For dynamic calculations, we use \( 100 \times 100 \) k-points and \( \omega \) grids from \(-30 \) eV to 30 eV with 600 points.

In Fig. 7 (b) we show the dependence of the absolute band gap changes for WS$_2$ for different dielectric constants on the vacuum height of the underlying \( G_0 W_0 \) calculation for the freestanding monolayer. In these \( G_0 W_0 \) calculations the quasi-particle band gap is underestimated but slowly converges with larger vacuum height. However, we see nearly no influence on the absolute band gap changes thus we chose \( c = 20 \) Å for all investigated TMDCs.
FIG. 7. (a) Convergence of the $G\Delta W$ band gap for $\varepsilon_{sub} = 100$ and WS$_2$ depending on the k-grid and (b) convergence of the absolute band gap difference depending on the vacuum height included in G$_0$W$_0$ calculations.
de Groot, and A. Wold, Physical Review B 35, 6195 (1987).

51 W. Schutte, J. D. Boer, and F. Jellinek, Journal of Solid State Chemistry 70, 207 (1987).

52 G. Schönhoff, M. Rösner, R. E. Groenewald, S. Haas, and T. O. Wehling, Physical Review B 94, 134504 (2016).

53 A. Emelyanenko and L. Boinovich, Journal of Physics: Condensed Matter 20, 494227 (2008).

54 L. Wang, Y. Pu, A. K. Soh, Y. Shi, and S. Liu, AIP Advances 6, 125126 (2016).

55 A. Laturia, M. L. V. de Put, and W. G. Vandenberghe, npj 2D Materials and Applications 2, 6 (2018).