Supplemental Material – Optical classification of excitonic phases in molecular functionalized atomically-thin semiconductors

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I. HAMILTONIAN

Due to the periodic arrangement of the molecules, the molecular operators of the lowest unoccupied orbital c of molecule ν can be transformed to a Bloch basis $c_{\mathbf{k}} = \sum_\nu \exp(-i\mathbf{k}\cdot\mathbf{R}_\nu)c_\nu/\sqrt{N_\mathrm{m}}$ with N_m the number of molecular unit cells and wave vector $\mathbf{k}$[1–3]. At the same time, valence band electrons in the TMDC layer are described by operators $v_{\mathbf{k}}$. In this notation, we can construct a many-particle Hamiltonian, which is parameterized from electronic structure *ab initio* calculations:

$$H = \sum_{\lambda,\mathbf{k}} \varepsilon_{\lambda,\mathbf{k}} \lambda^\dagger_{\mathbf{k}}\lambda_{\mathbf{k}} + ie_0 \sum_{\lambda,\mathbf{k}} \mathbf{E}(t)\cdot(\nabla_{\mathbf{k}}\lambda^\dagger_{\mathbf{k}})\lambda_{\mathbf{k}} + \hbar\sum_{\mathbf{k}} \Omega_{\mathbf{k}}(t)\left(v^\dagger_{\mathbf{k}}c_{\mathbf{k}} + c^\dagger_{\mathbf{k}}v_{\mathbf{k}}\right) + \frac{1}{2}\sum_{\substack{\lambda,\lambda',\nu,\nu'\\ \mathbf{k},\mathbf{k}',\mathbf{q}}} V^{\lambda\nu\nu'\lambda'}_{\mathbf{k},\mathbf{k}',\mathbf{q}}\ \lambda^\dagger_{\mathbf{k}+\mathbf{q}}\nu^\dagger_{\mathbf{k}'-\mathbf{q}}\nu'_{\mathbf{k}'}\lambda'_{\mathbf{k}}. \quad (1)$$

The first term describes the free kinetic energy. The single-particle energies are $\varepsilon_{c,\mathbf{k}} = E_G$ and $\varepsilon_{v,\mathbf{k}} = \hbar^2\mathbf{k}^2/2m$ with effective hole mass m. The second and third term describe intra- and interband transitions, respectively. The last term includes Coulomb interaction. To account for inter- and intraband renormalization effects and exciton formation we can restrict the band indices to the combinations of: all band indices correspond to valence or conduction band and to even numbers of valence and conduction band indices. Uneven numbers of band indices would describe Meitner-Auger processes. However, since valence and conduction band are in different layers, the Meitner-Auger process would require a large wave function overlap to significantly contribute and can therefore be neglected[4]. Together with a random phase approximation for electronic occupations $\langle\lambda^\dagger_{\mathbf{k}}\lambda_{\mathbf{k}'}\rangle \to \langle\lambda^\dagger_{\mathbf{k}}\lambda_{\mathbf{k}'}\rangle\delta_{\mathbf{k},\mathbf{k}'}$ we obtain the Hartree-Fock Hamiltonian

$$\begin{aligned}
H =& \sum_{\mathbf{k}}\left(\varepsilon_{c,\mathbf{k}} + \sum_{\mathbf{k}'} V^{\mathrm{mol}}_{\mathbf{0}} f_{c,\mathbf{k}'} + \sum_{\mathbf{k}'} V_{\mathbf{0}} f_{v,\mathbf{k}'} - \sum_{\mathbf{k}'} V^{\mathrm{mol}}_{\mathbf{k}-\mathbf{k}'} f_{c,\mathbf{k}'} - \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} f_{v,\mathbf{k}'}\right) c^\dagger_{\mathbf{k}}c_{\mathbf{k}} \\
&+ \sum_{\mathbf{k}}\left(\varepsilon_{v,\mathbf{k}} + \sum_{\mathbf{k}'} V^{\mathrm{WS}_2}_{\mathbf{0}} f_{v,\mathbf{k}'} + \sum_{\mathbf{k}'} V_{\mathbf{0}} f_{c,\mathbf{k}'} - \sum_{\mathbf{k}'} V^{\mathrm{WS}_2}_{\mathbf{k}-\mathbf{k}'} f_{v,\mathbf{k}'} - \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'} f_{c,\mathbf{k}'}\right) v^\dagger_{\mathbf{k}}v_{\mathbf{k}} \\
&+ ie_0\mathbf{E}(t)\cdot\sum_{\lambda,\mathbf{k}}\nabla_{\mathbf{k}}\lambda^\dagger_{\mathbf{k}}\lambda_{\mathbf{k}} \\
&- \sum_{\mathbf{k}}\left(\sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'}p^*_{\mathbf{k}'} - \mathbf{d}_{\mathbf{k}}\cdot\mathbf{E}(t)\right) v^\dagger_{\mathbf{k}}c_{\mathbf{k}} - \sum_{\mathbf{k}}\left(\sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'}p_{\mathbf{k}'} - \mathbf{d}^*_{\mathbf{k}}\cdot\mathbf{E}(t)\right) c^\dagger_{\mathbf{k}}v_{\mathbf{k}} \quad (2)\\
=& \sum_{\lambda,\mathbf{k}}\tilde{\varepsilon}_{\lambda,\mathbf{k}}\lambda^\dagger_{\mathbf{k}}\lambda_{\mathbf{k}} - \sum_{\mathbf{k}}\Delta_{\mathbf{k}}\left(v^\dagger_{\mathbf{k}}c_{\mathbf{k}} + c^\dagger_{\mathbf{k}}v_{\mathbf{k}}\right) + ie_0\sum_{\lambda,\mathbf{k}}\mathbf{E}(t)\cdot(\nabla_{\mathbf{k}}\lambda^\dagger_{\mathbf{k}})\lambda_{\mathbf{k}} + \hbar\sum_{\mathbf{k}}\Omega_{\mathbf{k}}(t)\left(v^\dagger_{\mathbf{k}}c_{\mathbf{k}} + c^\dagger_{\mathbf{k}}v_{\mathbf{k}}\right). \quad (3)
\end{aligned}$$

which reproduces the semiconductor Bloch equations in the Hartree-Fock limit, including effects as exciton formation or band gap renormalization. The single-particle energies $\tilde{\varepsilon}_{\lambda,\mathbf{k}}$ are renormalized by Hartree-Fock contributions of intra- and interlayer Coulomb interaction, which contain the carrier occupation $f_{\lambda,\mathbf{k}} = \langle\lambda^\dagger_{\mathbf{k}}\lambda_{\mathbf{k}}\rangle$ in TMDC and molecule layer and $\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}-\mathbf{k}'}p_{\mathbf{k}'}$ accounts for the formation of bound excitons and corresponds to the built up of a macroscopic coherence in the EI state. The microscopic transitions are defined as $p_{\mathbf{k}} = \langle v^\dagger_{\mathbf{k}}c_{\mathbf{k}}\rangle$ and $V_{\mathbf{k}}$ denotes the interlayer Coulomb potential[5]. The last two terms include light-matter interaction consisting of intra- and interband transitions. The latter are determined by the Rabi frequency $\Omega_{\mathbf{k}} = \mathbf{d}_{\mathbf{k}}\cdot\mathbf{E}(t)/\hbar$ with electronic dipole moment $\mathbf{d}_{\mathbf{k}}$ and electric field $\mathbf{E}(t)$. In this manuscript, we use the band gap energy as parameter, tunable by a static external additional out-of-plane electric field via the Stark effect[6]. This tuning enables different electronic phases of the heterostructure. Since the excitonic insulator phase results from a spontaneous formation of excitons, we first focus on the ground state calculation in absence of an external exciting optical field.

The Hamiltonian is then diagonalized with a Bogoliubov transformation. The new ground state is given by[7]

$$|\tilde{\Psi}_0\rangle = \Pi_{\mathbf{k}}\left(u^*_{\mathbf{k}} - w^*_{\mathbf{k}}c^\dagger_{\mathbf{k}}v_{\mathbf{k}}\right)|\Psi_0\rangle = \Pi_{\mathbf{k}}\alpha^\dagger_{\mathbf{k}}|0\rangle \quad (4)$$

with $|\Psi_0\rangle = \Pi_{\mathbf{k}} v_{\mathbf{k}}^\dagger |0\rangle$ as the conventional semiconducting ground state constructed from the vacuum state $|0\rangle$. The coherence factors $|w_{\mathbf{k}}|^2$ and $|u_{\mathbf{k}}|^2$ describe the probabilities that the pair state is occupied or unoccupied, respectively. The diagonalization yields the coherence factors

$$|u_{\mathbf{k}}|^2 = \frac{1}{2}\left(1 + \frac{\Sigma_{\mathbf{k}}}{\sqrt{\Sigma_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2}}\right), \quad \text{and} \quad |w_{\mathbf{k}}|^2 = \frac{1}{2}\left(1 - \frac{\Sigma_{\mathbf{k}}}{\sqrt{\Sigma_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2}}\right). \tag{5}$$

Finally, we define the Coulomb potential

$$V_{\mathbf{q}}^{ll'} = \frac{e_0^2}{2\epsilon_0 A|\mathbf{q}|\epsilon_{\mathbf{q}}^{ll'}}; \quad \epsilon_{\mathbf{q}}^{ll'} = \begin{cases} \epsilon_{\mathbf{q}}, & l \neq l' \\ \epsilon_{\mathbf{q}}^i, & l = l' \equiv i \end{cases} \tag{6}$$

with $i = \{0, 1\}$ for molecular and TMDC layer. The dielectric functions read

$$\epsilon_{\mathbf{q}} = \kappa g_{|\mathbf{q}|}^0 g_{|\mathbf{q}|}^1 f_{|\mathbf{q}|} \quad \text{and} \quad \epsilon_{\mathbf{q}}^i = \frac{\kappa g_{|\mathbf{q}|}^{1-i} f_{|\mathbf{q}|}}{\cosh(\delta_{1-i}|\mathbf{q}|/2) h_{|\mathbf{q}|}^i} \tag{7}$$

with the abbreviations

$$f_{\mathbf{q}} = 1 + \frac{1}{2}\left((\frac{\kappa_0}{\kappa} + \frac{\kappa}{\kappa_0})\tanh(\delta_0|\mathbf{q}|) + (\frac{\kappa_1}{\kappa} + \frac{\kappa}{\kappa_1})\tanh(\delta_1|\mathbf{q}|) + (\frac{\kappa_0}{\kappa_1} + \frac{\kappa_1}{\kappa_0})\tanh(d_0|\mathbf{q}|)\tanh(\delta_1|\mathbf{q}|)\right) \tag{8}$$

$$h_{\mathbf{q}}^i = 1 + \frac{\kappa}{\kappa_i}\tanh(\delta_i|\mathbf{q}|) + \frac{\kappa}{\kappa_{1-i}}\tanh(\delta_{1-i}|\mathbf{q}|/2) + \frac{\kappa_i}{\kappa_{1-i}}\tanh(\delta_i|\mathbf{q}|)\tanh(\delta_{1-i}|\mathbf{q}|/2) \tag{9}$$

$$g_{\mathbf{q}}^i = \frac{\cosh(\delta_i|\mathbf{q}|)}{\cosh(\delta_{1-i}|\mathbf{q}|/2)}\left(1 + \frac{\kappa}{\kappa_i}\tanh(\delta_i|\mathbf{q}|/2)\right). \tag{10}$$

The parameters are $\kappa_i = \sqrt{\epsilon_\parallel^i \epsilon_\perp^i}$ and κ for the dielectric background, $\alpha_i = \sqrt{\epsilon_\parallel^i/\epsilon_\perp^i}$, $\delta_i = \alpha_i d_i$ with the layer thickness d_i.

II. EQUATIONS OF MOTION

The macroscopic polarization is defined as $\mathbf{P}(t) = -\delta H_{lm}/\delta \mathbf{E}(t)$ with the light-matter Hamiltonian H_{lm}. Already in excitonic basis, the macroscopic polarization reads

$$\mathbf{P}(t) = -\sum_{\mu,\mathbf{k}}\left(f_{\mathbf{k}}^{(0)}\varphi_{\mu,\mathbf{k}}\mathbf{d}_{\mathbf{k}} + ie_0\varphi_{\mu,\mathbf{k}}^*\nabla_{\mathbf{k}}p_{\mathbf{k}}^{(0)}\right)P_\mu + ie_0\sum_{\lambda,\mathbf{k}}[\nabla_{\mathbf{k}}\lambda_{\mathbf{k}}^\dagger]\lambda_{\mathbf{k}} \tag{11}$$

from the macroscopic polarization we can calculate the optical current

$$\mathbf{j}(t) = -\sum_{\mu,\mathbf{k}}\left(\mathbf{d}_{\mathbf{k}}\varphi_{\mu,\mathbf{k}}f_{\mathbf{k}}^{(0)} + ie_0\varphi_{\mu,\mathbf{k}}\nabla_{\mathbf{k}}p_{\mathbf{k}}^{(0)}\right)\frac{d}{dt}P_\mu(t) + e_0\sum_{\mathbf{k}}\mathbf{v}_{\mathbf{k}}F_{v,\mathbf{k}}^{(1)}(t) \tag{12}$$

$$\mathbf{j}(\omega) = -\sum_{\mu,\mathbf{k}}\left(\mathbf{d}_{\mathbf{k}}\varphi_{\mu,\mathbf{k}}f_{\mathbf{k}}^{(0)} + ie_0\varphi_{\mu,\mathbf{k}}\nabla_{\mathbf{k}}p_{\mathbf{k}}^{(0)}\right)i\omega P_\mu(\omega) + e_0\sum_{\mathbf{k}}\mathbf{v}_{\mathbf{k}}F_{v,\mathbf{k}}^{(1)}(\omega) \tag{13}$$

where we introduced the particle velocity $\mathbf{v}_{\mathbf{k}} = \hbar\mathbf{k}/m$ and Fourier transformed to get from Eq. (12) to Eq. (13). Since the molecule electrons are infinitely heavy they do not contribute to the current that only the valence band electrons $F_{v,\mathbf{k}_\parallel}^{(1)}$ are relevant. We derive the equations of motion for the optical excitations, which read

$$i\hbar\frac{d}{dt}p_{\mathbf{k}} = (2\Sigma_{\mathbf{k}} + ie_0\mathbf{E}(t)\cdot\nabla_{\mathbf{k}})\,p_{\mathbf{k}} - \Delta_{\mathbf{k}}f_{\mathbf{k}} + \hbar\Omega_{\mathbf{k}}f_{\mathbf{k}} \tag{14}$$

$$i\hbar\frac{d}{dt}f_{\mathbf{k}} = 2i\Im\mathrm{m}\left(\Delta_{\mathbf{k}}p_{\mathbf{k}}\right) + e_0\mathbf{E}(t)\cdot\nabla_{\mathbf{k}}f_{\mathbf{k}} \tag{15}$$

with $2\Sigma_{\mathbf{k}} = \tilde{\varepsilon}_{c,\mathbf{k}} - \tilde{\varepsilon}_{v,\mathbf{k}}$ and inversion $f_{\mathbf{k}} = f_{v,\mathbf{k}} - f_{c,\mathbf{k}}$. Then, we expand the polarization and density into orders of the exciting electric field

$$p_{\mathbf{k}} = p_{\mathbf{k}}^{(0)} + p_{\mathbf{k}}^{(1)} + \mathcal{O}(2) \tag{16}$$

$$f_{\mathbf{k}} = f_{\mathbf{k}}^{(0)} + f_{\mathbf{k}}^{(1)} + \mathcal{O}(2). \tag{17}$$

Staying in the first order of the electric field the HIOS Bloch equation reads

$$i\hbar\frac{d}{dt}p_{\mathbf{k}}^{(1)} = 2\Sigma_{\mathbf{k}}^{(0)}p_{\mathbf{k}}^{(1)} - \Delta_{\mathbf{k}}^{(1)}f_{\mathbf{k}}^{(0)} + 2\Sigma_{\mathbf{k}}^{(1)}p_{\mathbf{k}}^{(0)} - \Delta_{\mathbf{k}}^{(0)}f_{\mathbf{k}}^{(1)} + \hbar\Omega_{\mathbf{k}}f_{\mathbf{k}}^{(0)} + ie_0\mathbf{E}(t)\cdot\nabla_{\mathbf{k}}p_{\mathbf{k}}^{(0)} \tag{18}$$

$$i\hbar\frac{d}{dt}f_{\mathbf{k}}^{(1)} = 2i\Im\left(\Delta_{\mathbf{k}}^{(0)}p_{\mathbf{k}}^{(1)} + \Delta_{\mathbf{k}}^{(1)}p_{\mathbf{k}}^{(0)}\right) + ie_0\mathbf{E}(t)\cdot\nabla_{\mathbf{k}}f_{\mathbf{k}}^{(0)}. \tag{19}$$

Since $p_{\mathbf{k}}^{(0)}$ and $f_{\mathbf{k}}^{(0)}$ describe the ground state their dynamics vanish. The first two terms of Eq. (18) correspond to the semiconductor Bloch equation. The second two terms are new and couple ground state distributions and excited quantities. The last two terms describe the optical excitation with interband source with included Pauli blocking[8] and intraband source, respectively. The coupling induced by the third and fourth term can be resolved via the transformation[9]

$$P_{\mathbf{k}}^{(1)} = \frac{E_{\mathbf{k}}+\Sigma_{\mathbf{k}}^{(0)}}{E_{\mathbf{k}}}p_{\mathbf{k}}^{(1)} - \frac{E_{\mathbf{k}}-\Sigma_{\mathbf{k}}^{(0)}}{E_{\mathbf{k}}}p_{\mathbf{k}}^{*(1)} - \frac{\Delta_{\mathbf{k}}^{(0)}}{E_{\mathbf{k}}}f_{\mathbf{k}}^{(1)} \tag{20}$$

$$F_{\mathbf{k}}^{(1)} = \frac{\Delta_{\mathbf{k}}^{(0)}}{E_{\mathbf{k}}}\left(p_{\mathbf{k}}^{(1)} + p_{\mathbf{k}}^{*(1)}\right) + \frac{\Sigma_{\mathbf{k}}^{(0)}}{E_{\mathbf{k}}}f_{\mathbf{k}}^{(1)}. \tag{21}$$

We obtain

$$i\hbar\frac{d}{dt}P_{\mathbf{k}}^{(1)} = 2E_{\mathbf{k}}P_{\mathbf{k}}^{(1)} - \sum_{\mathbf{k}'}V_{\mathbf{k}-\mathbf{k}'}P_{\mathbf{k}'}^{(1)} + \hbar\Omega_{\mathbf{k}}f_{\mathbf{k}}^{(0)} + ie_0\mathbf{E}(t)\cdot\nabla_{\mathbf{k}}p_{\mathbf{k}}^{(0)} \tag{22}$$

$$i\hbar\frac{d}{dt}F_{\mathbf{k}}^{(1)} = ie_0\mathbf{E}(t)\cdot\nabla_{\mathbf{k}}f_{\mathbf{k}}^{(0)} \tag{23}$$

We can identify the Bogoliubov-Wannier equation

$$2E_{\mathbf{k}}\varphi_{\mu,\mathbf{k}} - \sum_{\mathbf{k}'}V_{\mathbf{k}-\mathbf{k}'}\varphi_{\mu,\mathbf{k}'} = E_\mu\varphi_{\mu,\mathbf{k}} \tag{24}$$

which yields the excitonic equations

$$i\hbar\frac{d}{dt}P_{\mu}^{(1)} = E_\mu P_\mu^{(1)} + \sum_{\mathbf{k}}f_{\mathbf{k}}^{(0)}\varphi_{\mu,\mathbf{k}}^*\hbar\Omega_{\mathbf{k}} + ie_0\mathbf{E}(t)\cdot\sum_{\mathbf{k}}\varphi_{\mu,\mathbf{k}}^*\nabla_{\mathbf{k}}p_{\mathbf{k}}^{(0)} \tag{25}$$

$$i\hbar\frac{d}{dt}F_{\mathbf{k}}^{(1)} = ie_0\mathbf{E}(t)\cdot\nabla_{\mathbf{k}}f_{\mathbf{k}}^{(0)} \tag{26}$$

Equation (25) can be Fourier transformed an inserted into Eq. (13). For the occupations we Fourier transform Eq. (26) with phenomenological dephasing and insert into Eq. (13), which yields for the last term

$$\mathbf{j}(\omega) = -e_0\sum_{\mathbf{k}}\mathbf{v}_{\mathbf{k}}\frac{ie_0\mathbf{E}(t)\nabla_{\mathbf{k}}f_{v,\mathbf{k}}^{(0)}}{\hbar\omega+i\gamma} = \left(-\frac{ie_0^2}{\hbar}\sum_{\mathbf{k}}\frac{\mathbf{v}_{\mathbf{k}}\otimes\nabla_{\mathbf{k}}f_{v,\mathbf{k}}^{(0)}}{\omega+i\gamma/\hbar}\right)\cdot\mathbf{E}(t) \tag{27}$$

Comparing with the definition of the current $\mathbf{j}(\omega) = -i\omega\epsilon_0\chi(\omega)\mathbf{E}(\omega)$ we can identify the scalar susceptibility

$$\chi(\omega) = -\frac{1}{\epsilon_0}\sum_{\mu}\frac{\mathbf{d}_\mu\otimes\mathbf{d}_\mu + \mathbf{j}_\mu\otimes\mathbf{j}_\mu}{\hbar\omega - E_\mu + i\gamma} + \frac{e_0^2}{\epsilon_0\hbar}\sum_{\mathbf{k}}\frac{\mathbf{v}_{\mathbf{k}}\otimes\nabla_{\mathbf{k}}f_{v,\mathbf{k}}^{(0)}}{\omega^2+i\omega\gamma/\hbar}. \tag{28}$$

In case that the electronic phase has a valence occupation $f_{v,\mathbf{k}}^{(0)}$ with Fermi edge, we can partially integrate the last term in Eq. (27) and find

$$\left(-\frac{ie_0^2}{\hbar}\sum_{\mathbf{k}}\frac{\mathbf{v}_{\mathbf{k}}\otimes\nabla_{\mathbf{k}}f_{v,\mathbf{k}}^{(0)}}{\omega+i\gamma/\hbar}\right)\cdot\mathbf{E}(t) = \frac{ie_0^2}{m}n_{el}\frac{1}{\omega+i\gamma/\hbar}\mathbf{E}(\omega) \tag{29}$$

where defined the carrier number $n_{el} = \sum_{\mathbf{k}}f_{v,\mathbf{k}}^{(0)}$. Again comparing with the definition of the optic current and assuming a perpendicular excitation we find the scalar susceptibility

$$\chi(\omega) = -\frac{1}{\epsilon_0}\sum_{\mu}\frac{|d_\mu|^2+|j_\mu|^2}{\hbar\omega-E_\mu+i\gamma} + \frac{\omega_{pl}^2}{\omega^2+i\omega\gamma/\hbar} \tag{30}$$

with the plasma frequency $\omega_{pl}^2 = e_0^2 n_{el}/\epsilon_0 m$.

III. OPTICAL SELECTION RULES OF EXCITONIC INSULATOR

Investigating the gap equation Eq. (1) of the main text we see that it corresponds to the Bogoliubov-Wannier equation with vanishing exciton binding energy. This suggests that also the ground state polarization could be projected onto the wave function acting as solution for $E_\mu = 0$: $p^{(0)}_{\mathbf{k}} = \sum_{\nu, E_\nu = 0} \varphi_{\nu,\mathbf{k}} p^{(0)}_\nu$. Then the momentum-gradient in the intraband matrix element acts onto the wave function. For a s-type ground state the angular derivative vanishes. Together with an analytical treatment of the angle-sum we obtain for the intraband source

$$j_\mu = e_0 \pi \mathbf{e} \cdot \sum_{\nu,k} \varphi^*_{\mu,k} \partial_k \varphi_{\nu,k} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \tag{31}$$

where the sign stands for $\mu = p_+$ and $\mu = p_-$ final states. These two final states exhibits a circular dichroismic selection rule, comparable to KK- and $\mathrm{K}^-\mathrm{K}^-$-excitons in monolayer TMDCs.

IV. ELECTRON-HOLE LIQUIDS

In this paragraph we discuss the different properties of EI and electron-hole liquid (EHLs) in two-dimensional semiconductors. Whereas the interlayer exciton in hybrids exist and can be detected at low densities[10], EHLs require a sufficient density to be stable.

The ground state of the here investigated heterostructure consists of interlayer exciton, where electron and hole are situated in spatially separated layers. Although being a direct-band gap system at the TMDC K point/molecule flat band, the interlayer character leads to long lifetimes compared to intralayer excitons. Such interlayer excitons can already exist at low densities. To estimate the exciton density n in units of the Bohr radius a_X[11], we calculate $n a_x^2 = a_X^2 \sum_{\mathbf{k}} |p^{(0)}_{\mathbf{k}}|^2$ and find a value of 0.02. The corresponding density $n = 3 \cdot 10^{12}/\mathrm{cm}^2$ lies below the Mott transition[12,13] and EHL formation threshold known for TMDC excitons[14]. Still, due to the comparably high density and the long lifetime, we need also to address the possibility of electron-hole liquids (EHL) next to the excitonic insulator (EI):

The EHL is a correlated electron-hole plasma. The EHL energy consists of three parts: kinetic, exchange, and correlation energy. The kinetic contribution corresponds to the kinetic energies of non-interacting electron and holes. The Fock term of the Coulomb interaction occurs in a mean-field approximation, the correlation occurs due to strong screening as a perturbative correction. It has been shown that the correlation energy is mainly mediated by large momentum transfer[15,16] and that in suspended monolayer TMDCs the main contribution to the binding energy of the EHL comes from kinetic and exchange energy[17]: For the EI considered here, the intravalley Coulomb interaction around the electronic K point is the dominant interaction. Here, short momentum transfer occurs and reduces the impact of the correlation energy. In particular, the combination with the molecular flat band favors small momentum transfer. However, also other configurations might occur: TMDCs exhibit a complex band structure with different side valleys. In our case, only the valence band of WS_2 is of interest with an energetic separation between the global maximum (K point) to other local maxima (Γ point) exceeding the exciton binding energy. In a possible multi-valley scenario also large momentum transfer could play a role and lead to a preference of the EHL state.

But even in this case (not considered here), the EHL corresponds to a non-equilibrium phase occurring at high electron-hole pair densities due to optical pumping In the here investigated heterostructure an excitonic ground state (EI) forms in absence of an optical pump. Therefore, the formation of an EHL would be a two-step processes. First, the formation of the EI (energetic favourable compared to a full valence and empty conduction band) followed by the transition into an EHL as energetic most favorable state due to the now present high electron-hole density.

On the other hand, A. Rustagi & A.F. Kemper[17] showed, that suspended monolayer MoS_2 exhibits a certain phase space, which consists of a mixture of EI and EHL; a possibility we do not want to exclude for the here investigated heterostructure.

We want to emphasize, that an optical absorption experiment should be able to clarify the nature of the phase. In the main manuscript we described the unique spectral signatures for semiconductor, metal, and EI. Despite the interlayer character of the exciton, the oscillator strength of an EI originates from *intraband* transitions and therefore contribute to a linear optical response. In contrast, the optical response of an EHL should originate from *interband* transitions. Therefore, a linear absorption experiment should also be able to distinguish between the EI and EHL phase.

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