Excitonic effects in the optoelectronic responses of two-dimensional semiconductors

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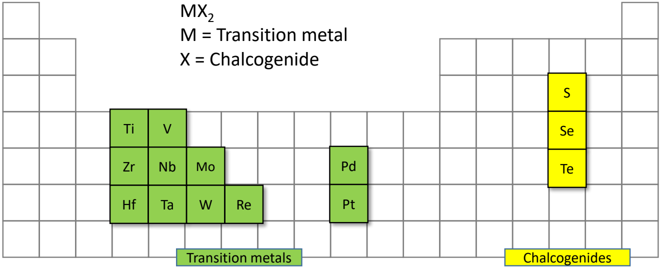
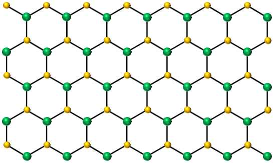
Outline

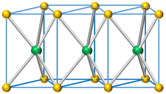
Transition metal dichalcogenide monolayers



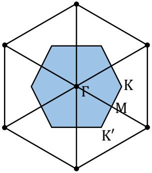
Top view



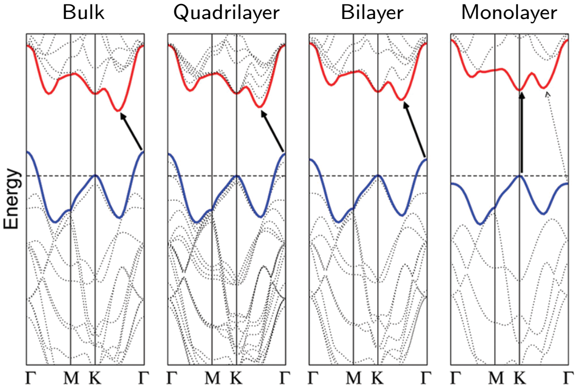
Side view



Reciprocal lattice
and 1st Brillouin zone



Transition metal dichalcogenide (TMD) monolayers are semiconductors with a direct band gap

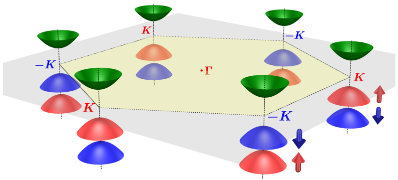


Ab initio band structures of bulk $\mathrm{MoS_2}$ and ultrathin $\mathrm{MoS_2}$ layers[1]

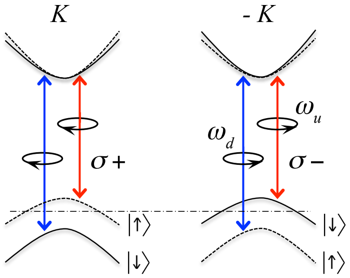
[1] Figure adapted from ref. A. Splendiani *et al.*, Nano Lett. **10**, 1271-1275 (2010)

Transition metal dichalcogenide monolayers

TMD monolayers have a large spin splitting at band valleys



Schematic drawing of the band structure at the band edges

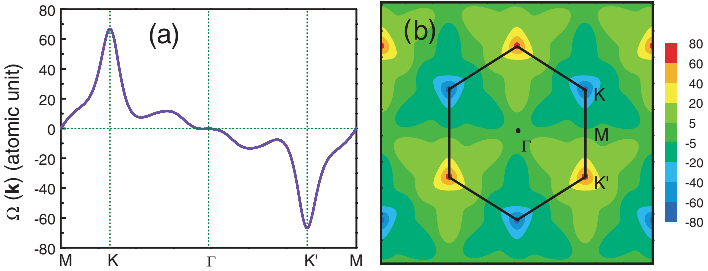


Valley and spin optical transition selection rules

Inversion asymmetry together with strong spin-orbit coupling (SOC) leads to a spin splitting of hundreds meV at the band valleys
$\Rightarrow$ Coupled spin and valley physics[2]

[2] Figures adapted from ref. D. Xiao *et al.*, Phys. Rev. Lett. **108**, 196802 (2012)

TMD monolayers possess interesting Berry curvature effects[3]



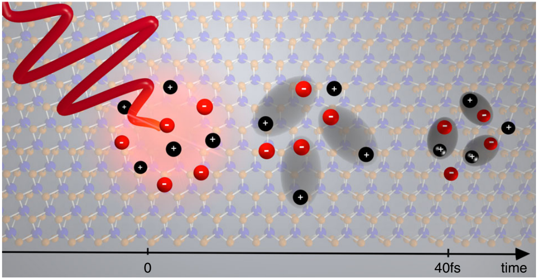
The Berry curvatures of monolayer $\mathrm{MoS_2}$ along the high-symmetry lines (a) and in 2D k-space (b)[4]

[3] Berry curvature is a local manifestation of the geometric phase properties of the wave functions in the parameter space

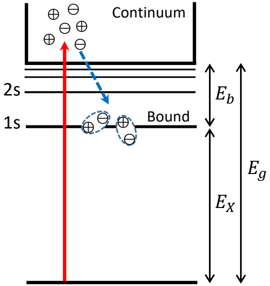
[4] W. Feng *et al.*, Phys. Rev. B **86**, 165108 (2012)

Exciton in 2D semiconductors

Exciton is a pair of electron and hole bound together by Coulomb attraction

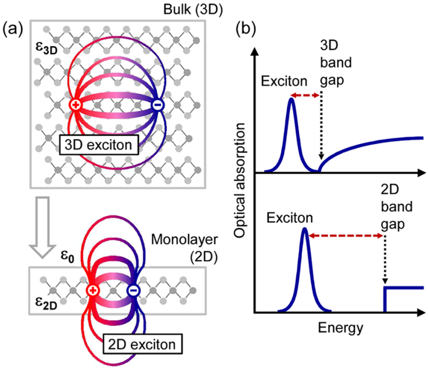


Exciton formation process after photo-injection of free electron-hole pairs[5]



[5] Figure adapted from ref. C. Trovatello *et al.*, Nat. Commun. **11**, 5277 (2020)

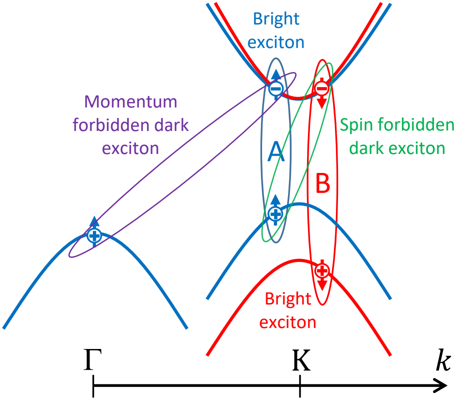
Exciton in 2D semiconductors



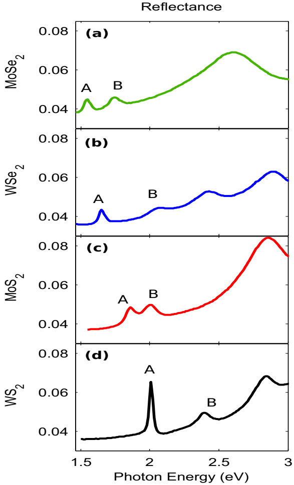
Strong quantum confinement and weak dielectric screening lead to an increase of exciton binding energy in semiconducting 2D materials, e.g. $E_b = 0.32 \pm 0.04$ eV for monolayer $\mathrm{WS_2}$[6], $E_b = 0.22 \pm 0.1$ eV for monolayer $\mathrm{MoS_2}$[7]

[6] Figure adapted from ref. A. Chernikov *et al.*, Phys. Rev. Lett. **113**, 076802 (2014)
[7] C. Zhang *et al.*, Nano Lett. **14**, 2443-2447 (2014)

Exciton in 2D semiconductors



Different exciton types in TMD monolayers



Measured optical response of TMD monolayers[8]

[8] Figure adapted from ref. Y. Li *et al.*, Phys. Rev. B **90**, 205422 (2014)

Electronic band structure

- Tight binding theory

$$\psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) = \sum_j C_{\mathbf{k}}^{\lambda}(j) \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_j(\mathbf{r}-\mathbf{R})$$

$$\sum_{j'} \left[H_{jj'}^{\mathrm{TB}}(\mathbf{k}) - E_{\mathbf{k}}^{\lambda} S_{jj'}(\mathbf{k}) \right] C_{\mathbf{k}}^{\lambda}(j') = 0$$

$$H_{jj'}^{\mathrm{TB}}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \langle \phi_j(\mathbf{r}) | \left[-\frac{\hbar^2 \nabla^2}{2m} + V \right] | \phi_{j'}(\mathbf{r}-\mathbf{R}) \rangle$$

- $\mathbf{k}\cdot\mathbf{p}$ theory

$$\psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_j C_{\mathbf{k}}^{\lambda}(j) u_j(\mathbf{r})$$

$$\sum_{j'} \left[H_{jj'}^{\mathbf{k}\cdot\mathbf{p}}(\mathbf{k}) - E_{\mathbf{k}}^{\lambda} \delta_{jj'} \right] C_{\mathbf{k}}^{\lambda}(j') = 0$$

$$H_{jj'}^{\mathbf{k}\cdot\mathbf{p}}(\mathbf{k}) = \langle u_j | \left[-\frac{\hbar^2 \nabla^2}{2m} + V \right] | u_{j'} \rangle + \frac{\hbar^2 k^2}{2m} \delta_{jj'} + \frac{\hbar}{m} \mathbf{k} \cdot \langle u_j | -i\hbar \boldsymbol{\nabla} | u_{j'} \rangle$$

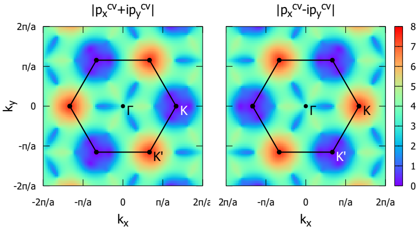
- DFT softwares, e.g. Quantum Espresso, provide $E_{\mathbf{k}}^{\lambda}$ and

$$\psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}}^{\lambda}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

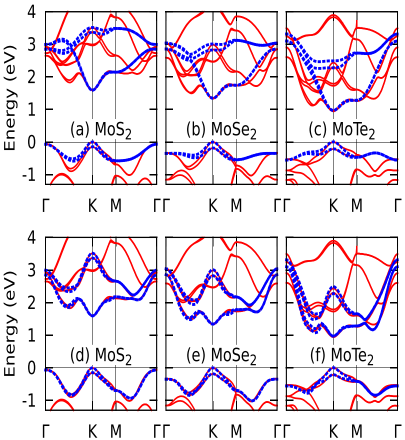
Three-band tight-binding model

The basis consists of three d-orbitals of the M atom:

$$|d_{z^2}\uparrow\rangle, |d_{xy}\uparrow\rangle, |d_{x^2-y^2}\uparrow\rangle,$$
$$|d_{z^2}\downarrow\rangle, |d_{xy}\downarrow\rangle, |d_{x^2-y^2}\downarrow\rangle$$



Optical matrix elements of monolayer $\mathrm{MoS_2}$



Bandstructure of $\mathrm{MoX_2}$ monolayers[9]

[9] G. B. Liu, *et al.*, Phys. Rev. B **88**, 085433 (2013)

Many-body Hamiltonian

Second quantized Hamiltonian of a crystal interacting with light:

$$H = H_0 + H_{\text{el-light}} + H_{\text{el-el}} + H_{\text{phonon}} + H_{\text{el-phonon}}$$

$$H_0 = \sum_{\lambda,\mathbf{k}} E^{\lambda}_{\mathbf{k}} a^{\lambda\dagger}_{\mathbf{k}} a^{\lambda}_{\mathbf{k}}$$

$$H_{\text{el-light}} = \frac{e}{m}\mathbf{A}(t)\cdot\sum_{\lambda,\lambda',\mathbf{k}} \mathbf{p}^{\lambda\lambda'}_{\mathbf{k}} a^{\lambda\dagger}_{\mathbf{k}} a^{\lambda'}_{\mathbf{k}}$$

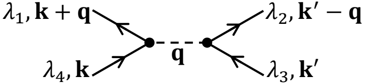
$$H_{\text{el-el}} = \frac{1}{2}\sum_{\lambda_1,\lambda_2,\lambda_3,\lambda_4,\mathbf{k},\mathbf{k}',\mathbf{q}} U^{\lambda_1\lambda_2\lambda_3\lambda_4}_{\mathbf{k},\mathbf{k}',\mathbf{q}} a^{\lambda_1\dagger}_{\mathbf{k}+\mathbf{q}} a^{\lambda_2\dagger}_{\mathbf{k}'-\mathbf{q}} a^{\lambda_3}_{\mathbf{k}'} a^{\lambda_4}_{\mathbf{k}}$$

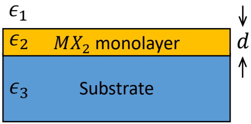
$$H_{\text{phonon}} = \sum_{\alpha,\mathbf{q}} \hbar\omega^{\alpha}_{\mathbf{q}} \left(b^{\alpha\dagger}_{\mathbf{q}} b^{\alpha}_{\mathbf{q}} + \frac{1}{2}\right)$$

$$H_{\text{el-phonon}} = \sum_{\alpha,\lambda,\lambda',\mathbf{k},\mathbf{q}} g^{\alpha,\lambda\lambda'}_{\mathbf{k}+\mathbf{q},\mathbf{k}} a^{\lambda\dagger}_{\mathbf{k}+\mathbf{q}} a^{\lambda'}_{\mathbf{k}} \left(b^{\alpha}_{\mathbf{q}} + b^{\alpha\dagger}_{-\mathbf{q}}\right)$$

Coulomb matrix elements

Coulomb matrix elements:





$$U_{\mathbf{k},\mathbf{k}',\mathbf{q}}^{\lambda_1\lambda_2\lambda_3\lambda_4} = \langle \psi_{\mathbf{k}+\mathbf{q}}^{\lambda_1}(\mathbf{r})\psi_{\mathbf{k}'-\mathbf{q}}^{\lambda_2}(\mathbf{r}')| \frac{1}{\epsilon(\mathbf{q})}\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}|\psi_{\mathbf{k}'}^{\lambda_3}(\mathbf{r}')\psi_{\mathbf{k}}^{\lambda_4}(\mathbf{r})\rangle$$

The effective dielectric constant of MX_2 monolayers can be described by[10]

$$\epsilon(\mathbf{q}) = \epsilon_2 \frac{1 - \frac{(1-\epsilon_2/\epsilon_1)(1-\epsilon_2/\epsilon_3)}{(1+\epsilon_2/\epsilon_1)(1+\epsilon_2/\epsilon_3)} e^{-2qd}}{\left[1 - \frac{1-\epsilon_2/\epsilon_1}{1+\epsilon_2/\epsilon_1} e^{-qd}\right]\left[1 - \frac{1-\epsilon_2/\epsilon_3}{1+\epsilon_2/\epsilon_3} e^{-qd}\right]}$$

[10] C. Zhang *et al.*, Phys. Rev. B **89**, 205436 (2014); L. V. Keldysh, Pis'ma Zh. Eksp. Teor. Fiz. 29, 716 (1979)

Equations of motion

Heisenberg equation of motion for $\langle a_{\mathbf{k}}^{\lambda\dagger} a_{\mathbf{k}}^{\lambda'} \rangle \equiv P_{\mathbf{k}}^{\lambda\lambda'}$ reads

$$\frac{d}{dt}\langle a_{\mathbf{k}}^{\lambda\dagger} a_{\mathbf{k}}^{\lambda'} \rangle = \frac{i}{\hbar}\langle [H, a_{\mathbf{k}}^{\lambda\dagger} a_{\mathbf{k}}^{\lambda'}] \rangle$$

Many-body interaction leads to an infinite hierarchy of equations

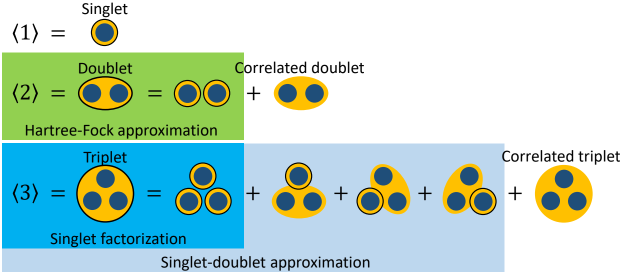
$$\begin{aligned}
\frac{d}{dt}\langle 1 \rangle &= T_1[\langle 1 \rangle] + V_1[\langle 2 \rangle] \\
\frac{d}{dt}\langle 2 \rangle &= T_2[\langle 2 \rangle] + V_2[\langle 3 \rangle] \\
\frac{d}{dt}\langle N \rangle &= T_N[\langle N \rangle] + V_N[\langle N+1 \rangle]
\end{aligned}$$

Cluster expansion approach:

$$\begin{aligned}
\langle 2 \rangle &= \langle 2 \rangle_{\mathrm{S}} + \Delta\langle 2 \rangle \\
\langle 3 \rangle &= \langle 3 \rangle_{\mathrm{S}} + \langle 1 \rangle \Delta\langle 2 \rangle + \Delta\langle 3 \rangle \\
\langle N \rangle &= \langle N \rangle_{\mathrm{S}} + \langle N-2 \rangle_{\mathrm{S}} \Delta\langle 2 \rangle + \langle N-4 \rangle_{\mathrm{S}} \Delta\langle 2 \rangle \Delta\langle 2 \rangle + ... \\
&\quad + \langle N-3 \rangle_{\mathrm{S}} \Delta\langle 3 \rangle + \langle N-5 \rangle_{\mathrm{S}} \Delta\langle 2 \rangle \Delta\langle 3 \rangle + ... + \Delta\langle N \rangle
\end{aligned}$$

Equations of motion

Visualization of the cluster expansion approach



One finds the general equation structure

$$\frac{d}{dt}\langle 1\rangle = T_1[\langle 1\rangle] + V_{1a}[\langle 2\rangle_{\mathrm{S}}] + V_{1b}[\Delta\langle 2\rangle]$$

$$\frac{d}{dt}\Delta\langle 2\rangle = T_2[\Delta\langle 2\rangle] + V_{2a}[\langle 3\rangle_{\mathrm{SD}}] + V_{2b}[\Delta\langle 3\rangle]$$

$$\frac{d}{dt}\Delta\langle 3\rangle = T_3[\Delta\langle 3\rangle] + V_{3a}[\langle 4\rangle_{\mathrm{SDT}}] + V_{3b}[\Delta\langle 4\rangle]$$

Multi-band semiconductor Bloch equations

Treating the Coulomb interaction in the cluster expansion approach up to the triplet level we obtain equations of motion for $P_{\mathbf{k}}^{\lambda\lambda'}$

$$\frac{d}{dt}P_{\mathbf{k}}^{\lambda\lambda'} = \frac{i}{\hbar}\left(E_{\mathbf{k}}^{\lambda} - E_{\mathbf{k}}^{\lambda'}\right)P_{\mathbf{k}}^{\lambda\lambda'} + i\sum_{\mu}\left(\Omega_{\mathbf{k}}^{\lambda'\mu}P_{\mathbf{k}}^{\lambda\mu} - \Omega_{\mathbf{k}}^{\mu\lambda}P_{\mathbf{k}}^{\mu\lambda'}\right)$$
$$+\frac{1}{\hbar}\sum_{\mu,\mu',\lambda'',\mathbf{k}',\mathbf{q}}\left[\left(U_{\mathbf{q}.\mathbf{k}',\mathbf{k}-\mathbf{q}}^{\lambda\mu\mu'\lambda''}c_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda'\mu\mu'\lambda''}\right)^{*} - U_{\mathbf{q},\mathbf{k}',\mathbf{k}-\mathbf{q}}^{\lambda'\mu\mu'\lambda''}c_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda\mu\mu'\lambda''}\right] + \left(\frac{d}{dt}P_{\mathbf{k}}^{\lambda\lambda'}\right)\Bigg|_{\text{el-phonon}}^{\text{scatt}}$$

$$\frac{d}{dt}c_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda\mu\mu'\lambda'} = \frac{i}{\hbar}\left(E_{\mathbf{k}}^{\lambda} + E_{\mathbf{k}'}^{\mu} - E_{\mathbf{k}'+\mathbf{q}}^{\mu'} - E_{\mathbf{k}-\mathbf{q}}^{\lambda'}\right)c_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda\mu\mu'\lambda'}$$
$$+ i\sum_{\nu}\left(\Omega_{\mathbf{k}-\mathbf{q}}^{\lambda'\nu}c_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda\mu\mu'\nu} + \Omega_{\mathbf{k}'+\mathbf{q}}^{\mu'\nu}c_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda\mu\nu\lambda'} - \Omega_{\mathbf{k}'}^{\nu\mu}c_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda\nu\mu'\lambda'} - \Omega_{\mathbf{k}}^{\nu\lambda}c_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\nu\mu\mu'\lambda'}\right)$$
$$+ S_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda\mu\mu'\lambda'} + D_{\mathbf{q},\mathbf{k}',\mathbf{k}}^{\lambda\mu\mu,\lambda'}$$

Generalized Rabi frequency:

$$\Omega_{\mathbf{k}}^{\lambda\lambda'} = \frac{1}{\hbar}\left[\frac{e}{m}\mathbf{A}(t)\cdot\mathbf{p}_{\mathbf{k}}^{\lambda\lambda'} - \sum_{\mu,\nu,\mathbf{k}'}U_{\mathbf{k},\mathbf{k}',\mathbf{k}'-\mathbf{k}}^{\mu\lambda\nu\lambda'}P_{\mathbf{k}'}^{\mu\nu}\right]$$

Multi-band semiconductor Bloch equations

Treating the electron-phonon interaction in the second-order Born-Markov level we have

$$\left(\frac{d}{dt}P_{\mathbf{k}}^{\lambda\lambda}\right)\Bigg|_{\text{el-phonon}}^{\text{scatt}} = \Gamma_{\lambda,\mathbf{k}}^{\text{in}}(1-P_{\mathbf{k}}^{\lambda\lambda}) - \Gamma_{\lambda,\mathbf{k}}^{\text{out}}P_{\mathbf{k}}^{\lambda\lambda}$$

$$\left(\frac{d}{dt}P_{\mathbf{k}}^{\lambda\lambda'}\right)\Bigg|_{\text{el-phonon}}^{\text{scatt}} = -\frac{P_{\mathbf{k}}^{\lambda\lambda'}(t)}{T_{\mathbf{k}}^{\lambda,\lambda'}}\,, \quad \lambda\neq\lambda'$$

$$\Gamma_{\lambda,\mathbf{k}}^{\text{in}} = \frac{2\pi}{\hbar}\sum_{\alpha,\mu,\mathbf{q}}\left|g_{\mathbf{k+q},\mathbf{k}}^{\alpha,\mu\lambda}\right|^2\left[\delta\big(E_{\mathbf{k+q}}^{\mu}-E_{\mathbf{k}}^{\lambda}-\hbar\omega_{\mathbf{q}}^{\alpha}\big)\big(N_{\mathbf{q}}^{\alpha}+1\big)+\delta\big(E_{\mathbf{k+q}}^{\mu}-E_{\mathbf{k}}^{\lambda}+\hbar\omega_{\mathbf{q}}^{\alpha}\big)N_{\mathbf{q}}^{\alpha}\right]P_{\mathbf{k+q}}^{\mu\mu}$$

$$\Gamma_{\lambda,\mathbf{k}}^{\text{out}} = \frac{2\pi}{\hbar}\sum_{\alpha,\mu,\mathbf{q}}\left|g_{\mathbf{k+q},\mathbf{k}}^{\alpha,\mu\lambda}\right|^2\left[\delta\big(E_{\mathbf{k+q}}^{\mu}-E_{\mathbf{k}}^{\lambda}-\hbar\omega_{\mathbf{q}}^{\alpha}\big)N_{\mathbf{q}}^{\alpha}+\delta\big(E_{\mathbf{k+q}}^{\mu}-E_{\mathbf{k}}^{\lambda}+\hbar\omega_{\mathbf{q}}^{\alpha}\big)\big(N_{\mathbf{q}}^{\alpha}+1\big)\right]\big(1-P_{\mathbf{k+q}}^{\mu\mu}\big)$$

$$\begin{aligned}T_{\mathbf{k}}^{\lambda,\lambda'} = {} & \frac{1}{\hbar}\sum_{\alpha,\mu,\mathbf{q}}\left|g_{\mathbf{k+q},\mathbf{k}}^{\alpha,\mu\lambda}\right|^2\left[\mathcal{D}\big(E_{\mathbf{k+q}}^{\mu}-E_{\mathbf{k}}^{\lambda'}-\hbar\omega_{\mathbf{q}}^{\alpha}\big)\big(N_{\mathbf{q}}+P_{\mathbf{k+q}}^{\mu\mu}\big)+\mathcal{D}\big(E_{\mathbf{k+q}}^{\mu}-E_{\mathbf{k}}^{\lambda'}+\hbar\omega_{\mathbf{q}}^{\alpha}\big)\big(N_{\mathbf{q}}^{\alpha}+1-P_{\mathbf{k+q}}^{\mu\mu}\big)\right] \\ & + \frac{1}{\hbar}\sum_{\alpha,\mu,\mathbf{q}}\left|g_{\mathbf{k},\mathbf{k+q}}^{\alpha,\lambda'\mu}\right|^2\left[\mathcal{D}\big(E_{\mathbf{k}}^{\lambda}-E_{\mathbf{k+q}}^{\mu}+\hbar\omega_{\mathbf{q}}^{\alpha}\big)\big(N_{\mathbf{q}}+P_{\mathbf{k+q}}^{\mu\mu}\big)+\mathcal{D}\big(E_{\mathbf{k}}^{\lambda}-E_{\mathbf{k+q}}^{\mu}-\hbar\omega_{\mathbf{q}}^{\alpha}\big)\big(N_{\mathbf{q}}^{\alpha}+1-P_{\mathbf{k+q}}^{\mu\mu}\big)\right]\end{aligned}$$

Optoelectronic responses

Electric field of a laser pulse can be described by

$$\mathbf{E}(t) = \hat{\mathbf{e}} E_{\mathrm{env}}(t) e^{i\omega_L t} + c.c$$

Solving the Multi-band semiconductor Bloch equations for $P_{\mathbf{k}}^{\lambda\lambda'}(t)$ with the initial condition

$$P_{\mathbf{k}}^{\lambda\lambda'}(t = -\infty) = \begin{cases} 1 & \lambda = \lambda' \in \mathrm{VB} \\ 0 & \text{otherwise} \end{cases}$$

we can calculate optoelectronic responses

Photocurrent:

$$\mathbf{J}(t) = -\frac{e}{m} \sum_{\lambda,\lambda',\mathbf{k}} \mathbf{p}_{\mathbf{k}}^{\lambda\lambda'} P_{\mathbf{k}}^{\lambda\lambda'}(t)$$

Macroscopic polarization:

$$\mathbf{P}(t) = e \sum_{\lambda,\lambda' \neq \lambda,\mathbf{k}} \boldsymbol{\xi}_{\mathbf{k}}^{\lambda\lambda'} P_{\mathbf{k}}^{\lambda\lambda'}(t)$$

Excitonic ballistic currents

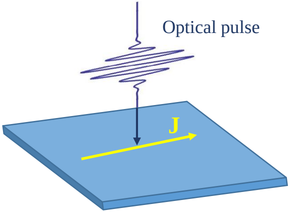
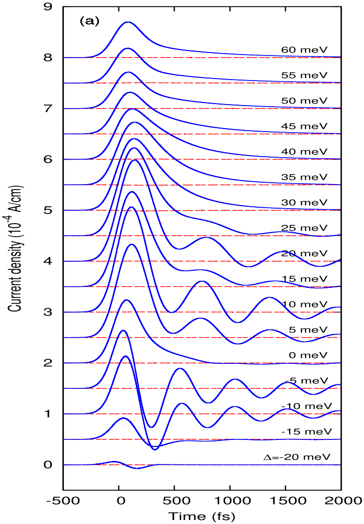


Illustration of the generation of photocurrent



Ballistic photocurrent in a GaAs quantum well[11]

[11] H. T. Duc *et al.*, Phys. Rev. B **100**, 045308 (2019)

Excitonic anomalous currents

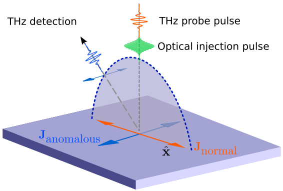


Illustration of the scheme for injection and detection of anomalous current[12]

[12] Figure adapted from ref. K. S. Virk and J. E. Sipe, Phys. Rev. Lett. **107**, 120403 (2011)

Summary