

Non-Equilibrium Green's Function Theory of Quantum Photovoltaic Devices

CECAM Workshop, Manchester, 25.6.2010 | U. Aeberhard, IEF-5: Photovoltaik, FZJ

Outline

- 1 Quantum photovoltaic devices
- 2 NEGF theory of QPV devices
- 3 Application example: carrier photogeneration and escape in SQW *pin*-diodes
- 4 Conclusions & outlook

Motivation

Low-dimensional absorbers in high efficiency PV

- Multi-junction cells: multiple band gaps
 - Intermediate band cell: absorption of high and low energy photons
 - Multiple exciton generation: $QE > 1$
 - Hot carrier solar cells: reduced thermalization losses
 - Fluorescent concentrator: spectral conversion
 - Quantum well solar cells: extended absorption range in single junction
- based on quantum effects in semiconductor nanostructures

Motivation

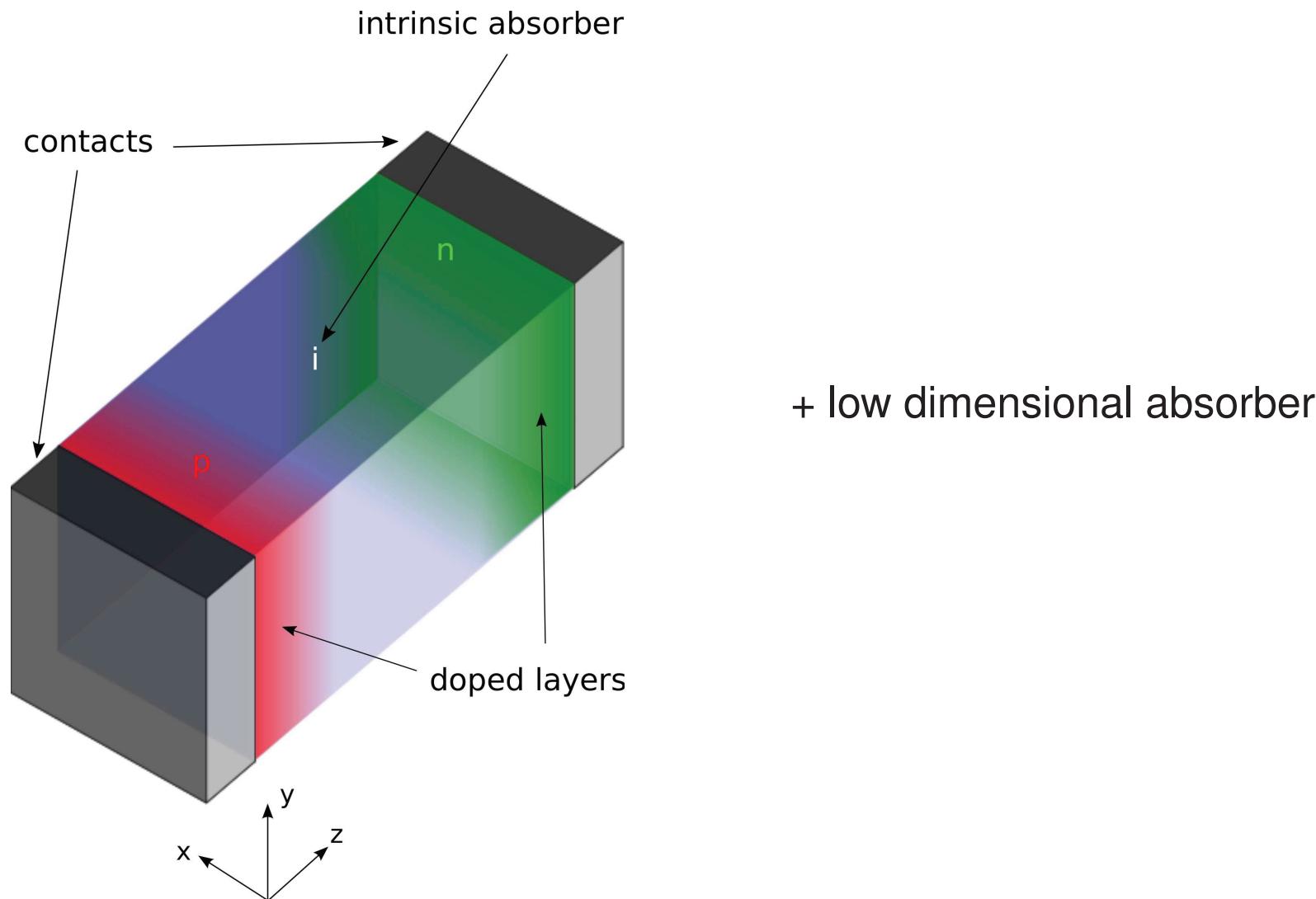
Low-dimensional absorbers in high efficiency PV

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- QW/QD-SL
- QD-SL
- QD, confinement
- QD, phonons
- QD
- QW

⇒ need quantum theory of photovoltaic processes in nanostructures

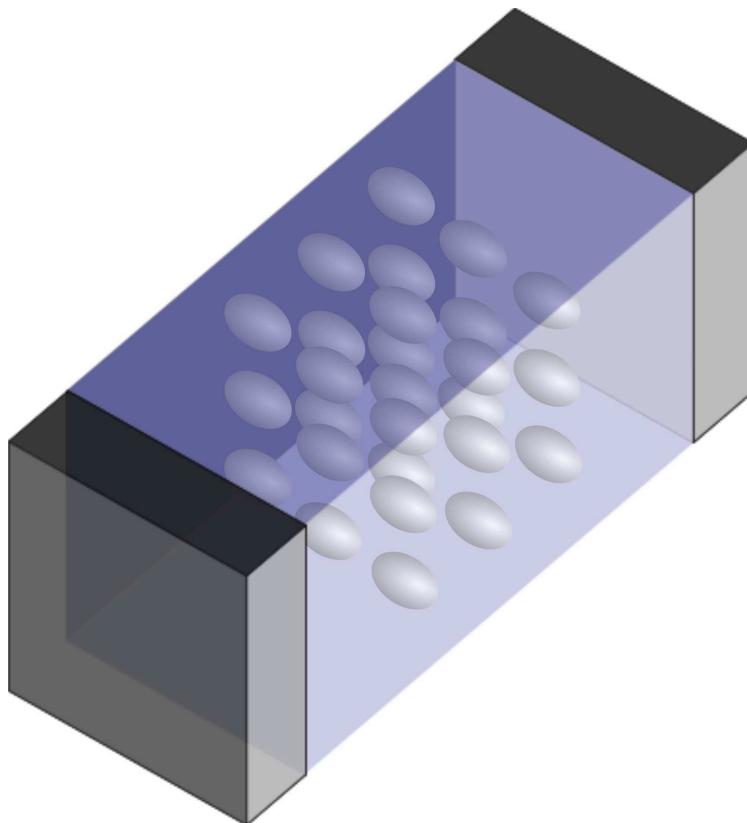
Quantum photovoltaic devices

Structure



Quantum photovoltaic devices

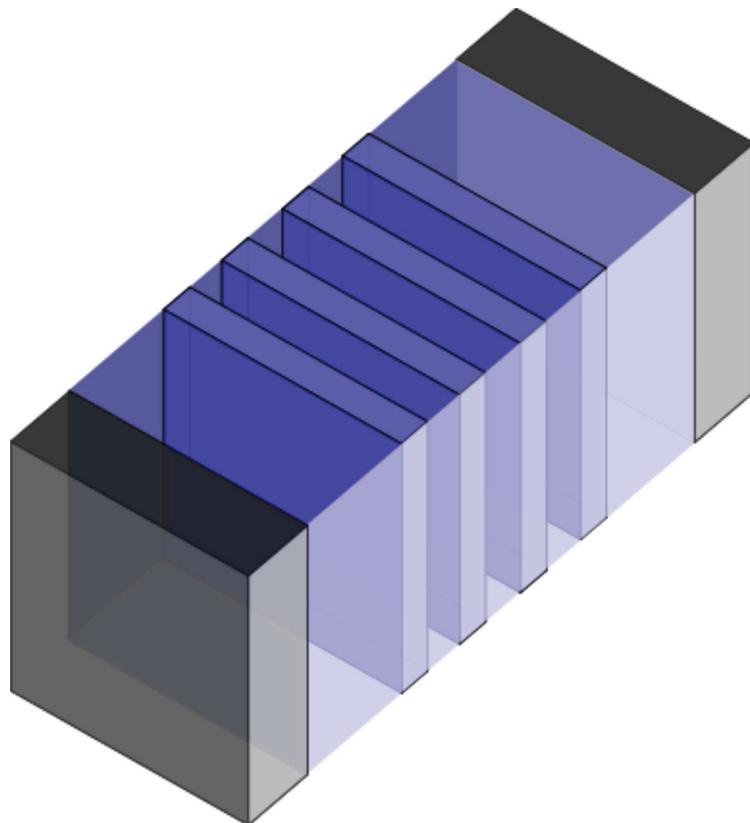
Structure



+ low dimensional absorber
→ quantum dots

Quantum photovoltaic devices

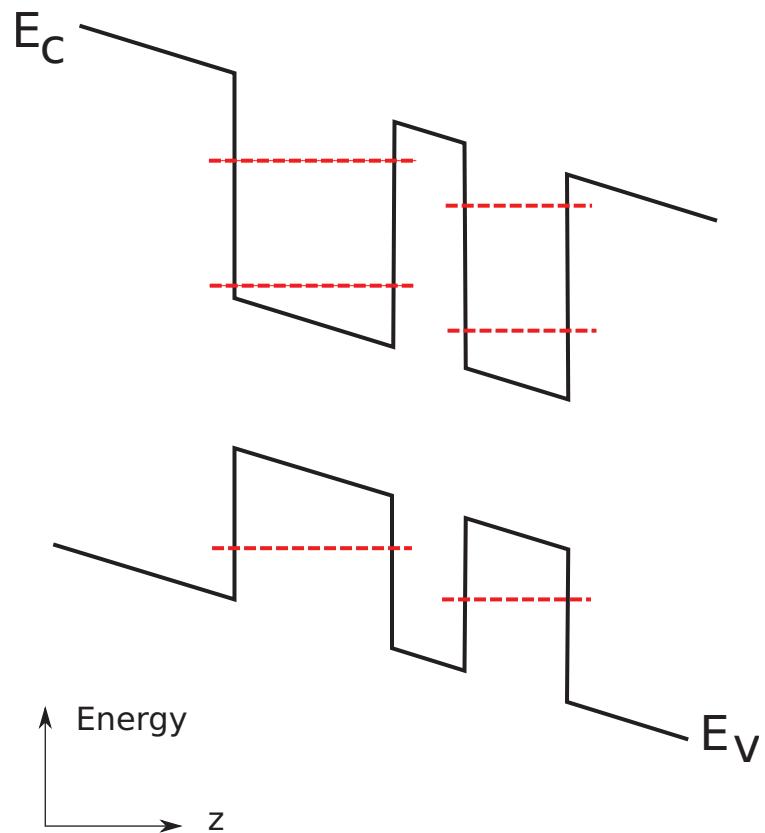
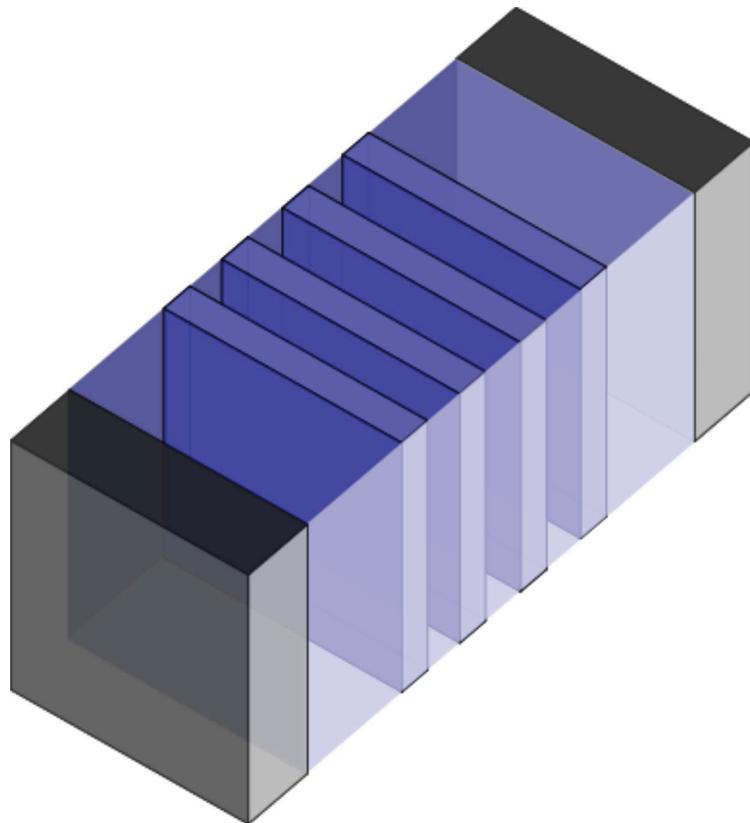
Structure



+ low dimensional absorber
→ quantum wells

Quantum photovoltaic devices

Structure



→ new (localized) states

Quantum photovoltaic devices

Processes

→ new (optoelectronic) processes

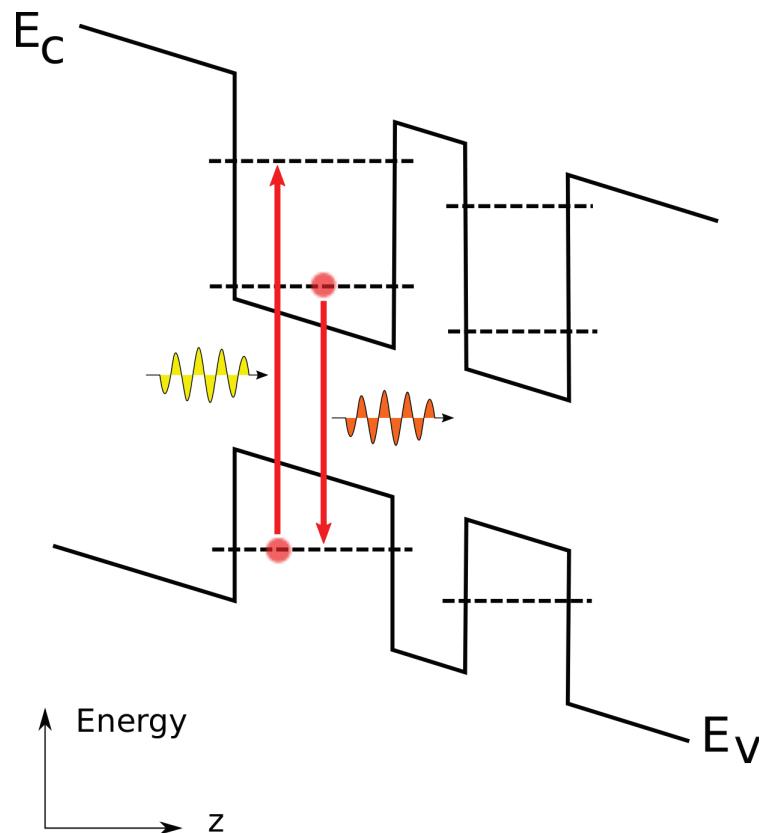
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- new radiative transitions: QW - QW, QW - continuum
- optical confinement, interference, scattering

electronic

- tunneling transport
- escape and capture QW-continuum
- nonradiative QW - transitions

model/theory?



Quantum photovoltaic devices

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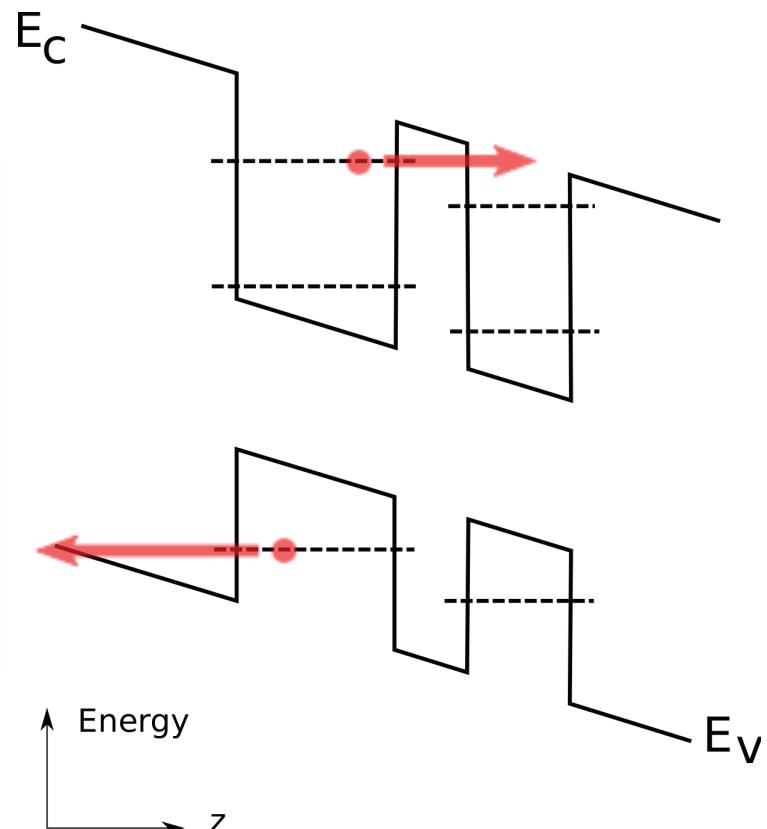
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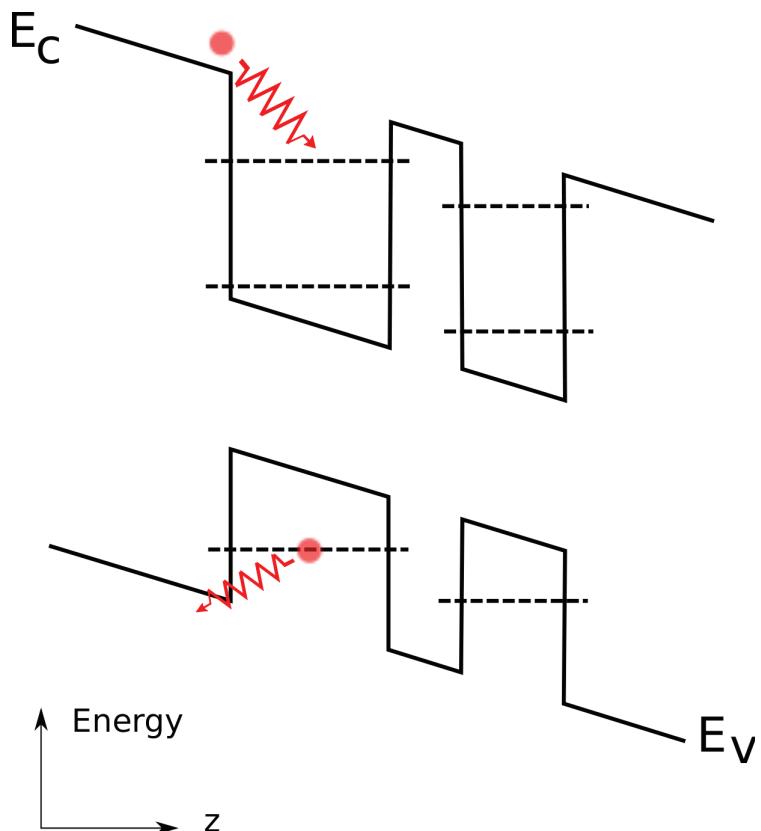
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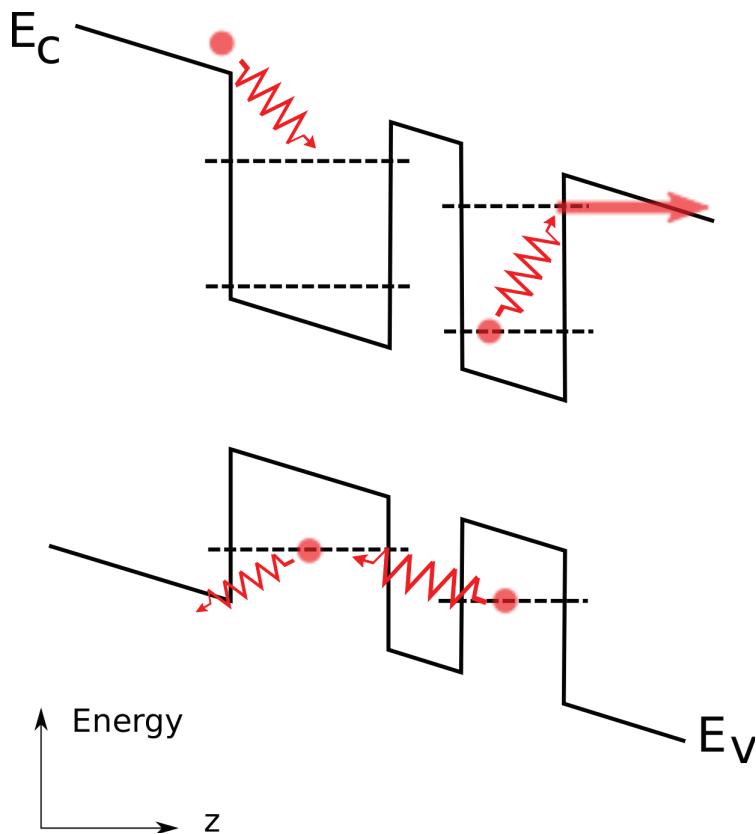
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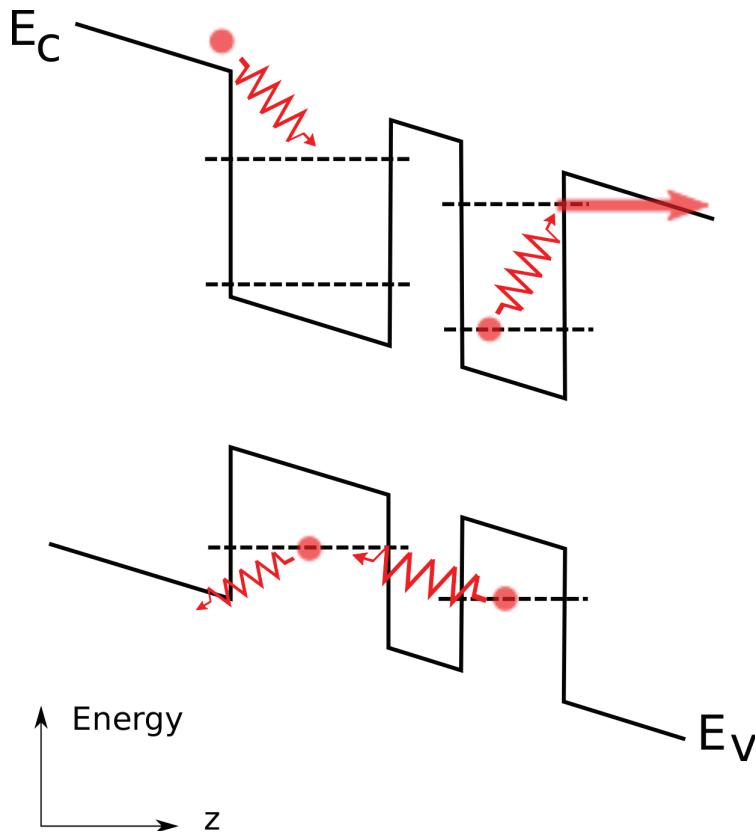
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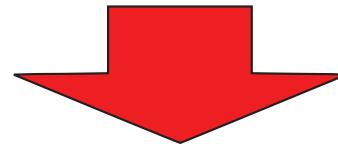
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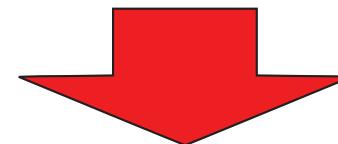
Theoretical challenges and model requirements

Conventional approach

generation/recombination
~ **localized** (low-D) states



charge transport
~ **extended** states



escape
capture

microscopic model

+

macroscopic model



hybrid approach: semiclassical transport theory with
detailed balance rates from microscopic models

⇒ Fitting model, but no coherent picture of **mechanisms**

Theoretical challenges and model requirements

New approach

- Instead: consistent microscopic theory of

- **optical** properties (inter- and subband transitions, cavity effects)
- **quantum transport** (tunneling, confinement, coherence)
- **open systems** (contacts, injection)
- **out of equilibrium** (bias, illumination)
- **scattering effects** (phonons, carriers, impurities, . . .)



quantum optics

+



quantum transport



microscopic quantum kinetic theory

Microscopic quantum kinetic approaches

- Electronic structure theories (\rightarrow states)

\rightarrow empirical:

- effective mass
- $k \cdot p$
- tight-binding
- pseudopotential

\rightarrow ab-initio:

- DFT

- Quantum kinetic theories (\rightarrow occupation)

- Wigner-function, density-matrix
- Non-equilibrium Green's function

Non-equilibrium Green's function theory of QPV

optical

photon field $\hat{\mathbf{A}}$

$$D_{ik}^{\gamma}(\underline{1}, \underline{2}) = -\frac{i}{\hbar} \langle \hat{A}_i(\underline{1}) \hat{A}_k(\underline{2}) \rangle_C$$

$$[(\overleftrightarrow{D}_0^{\gamma})^{-1} - \overleftrightarrow{\Pi}^{\gamma}] \otimes \overleftrightarrow{D}^{\gamma} = \overleftrightarrow{\delta}$$

$\overleftrightarrow{\Pi}$: transverse polarization

electronic

fermion field $\hat{\Psi}$

$$G(\underline{1}, \underline{2}) = -\frac{i}{\hbar} \langle \hat{\Psi}(\underline{1}) \hat{\Psi}^\dagger(\underline{2}) \rangle_C$$

$$[G_0^{-1} - \Sigma] \otimes G = \delta$$

$\Sigma = \Sigma_i + \Sigma_c$: scattering

$\Sigma_i = \Sigma_{e\gamma} + \Sigma_{ee} + \Sigma_{ep}$

vibrational

ionic displacement $\hat{\mathbf{U}}$

$$D_j^p(\underline{1}, \underline{2}) = -\frac{i}{\hbar} \langle \hat{U}_j^\dagger(\underline{1}) \hat{U}_j(\underline{2}) \rangle_C$$

$$[(D_{j,0}^p)^{-1} - \Pi_j^p] \otimes D_j^p = \delta$$

Π_j^p : lattice polarization

selfconsistent solution for

$$\mathcal{D}^{\gamma}, \Pi^{\gamma}, G, \Sigma, \mathcal{D}^p, \Pi^p$$

$$n(\underline{1}) = \lim_{2 \rightarrow 1} i\hbar G^<(\underline{1}, \underline{2}) \quad (\text{carrier density})$$

$$\mathbf{j}(\underline{1}) = \lim_{2 \rightarrow 1} \frac{\hbar^2}{2m_0} [\nabla(1) - \nabla(2)] G^<(\underline{1}, \underline{2}) \quad (\text{carrier current density})$$

$$S_i(\underline{1}) = \lim_{2 \rightarrow 1} \frac{i\hbar}{8\pi} \frac{\partial}{\partial t_1} \sum_{j \neq i} \left\{ \nabla_j(2) \left[\mathcal{D}_{ji}^{\gamma>}(\underline{1}, \underline{2}) + \mathcal{D}_{ji}^{\gamma<}(\underline{1}, \underline{2}) \right] - \nabla_i(2) \left[\mathcal{D}_{jj}^{\gamma>}(\underline{1}, \underline{2}) + \mathcal{D}_{jj}^{\gamma<}(\underline{1}, \underline{2}) \right] \right\}$$

$$\underline{1} \equiv (\mathbf{r}_1, t_1) \quad (\text{Poynting vector})$$

Non-equilibrium Green's function theory of QPV

Electronic conservation law

macroscopic photovoltaic balance equation

$$\nabla \cdot \mathbf{j}_c(\mathbf{r}) = \mathcal{G}_c(\mathbf{r}) - \mathcal{R}_c(\mathbf{r}), \quad \mathbf{j}_c(\mathbf{r}) = -\text{sgn}(q_c)\rho_c(\mathbf{r})\mu_c\nabla U(\mathbf{r}) - \rho_c(\mathbf{r})D_c\nabla\rho_c(\mathbf{r}), \quad c = e, h$$

microscopic conservation law (electronic)

$$\begin{aligned} & \lim_{2 \rightarrow 1} \left\{ i\hbar (\partial_{t_1} + \partial_{t_2}) G(12) + [H_0(\mathbf{r}_1) - H_0(\mathbf{r}_2)] G(12) \right\} \\ &= \lim_{2 \rightarrow 1} \int_C d^3 \mathbf{r} [\Sigma(13)G(32) - G(13)\Sigma(32)] \end{aligned}$$

→ steady state:

$$\begin{aligned} \nabla \cdot \mathbf{j}(\mathbf{r}) = -2e \int \frac{dE}{2\pi\hbar} \int d^3 r' \left[\begin{array}{l} \Sigma^R(\mathbf{r}, \mathbf{r}'; E)G^<(\mathbf{r}', \mathbf{r}; E) + \Sigma^<(\mathbf{r}, \mathbf{r}'; E)G^A(\mathbf{r}', \mathbf{r}; E) \\ -G^R(\mathbf{r}, \mathbf{r}'; E)\Sigma^<(\mathbf{r}', \mathbf{r}; E) - G^<(\mathbf{r}, \mathbf{r}'; E)\Sigma^A(\mathbf{r}', \mathbf{r}; E) \end{array} \right] \end{aligned}$$

$\equiv \mathcal{R}_{tot}^{el}(\mathbf{r})$: total local electronic rate (intra- and interband)

Non-equilibrium Green's function theory of QPV

Optical conservation law

microscopic conservation law (optical)

$$R_{\gamma}^{opt}(\hbar\omega) = \int d^3r \int d^3r' \left[\Pi_{\gamma}^{>}(\mathbf{r}, \mathbf{r}', \hbar\omega) - \Pi_{\gamma}^{<}(\mathbf{r}, \mathbf{r}', \hbar\omega) \right] D_{\gamma}^{<}(\mathbf{r}', \mathbf{r}, \hbar\omega) \quad \text{absorbed flux}$$

$$- \int d^3r \int d^3r' \Pi_{\gamma}^{<}(\mathbf{r}, \mathbf{r}', \hbar\omega) \hat{D}_{\gamma}(\mathbf{r}', \mathbf{r}, \hbar\omega) \quad \text{emitted flux}$$

total radiative rate \equiv interband current

$$\int d^3r R_{\gamma}^{el}(\mathbf{r}) = R_{\gamma} = \int d\hbar\omega R_{\gamma}^{opt}(\hbar\omega)$$

generation	\longleftrightarrow	absorption
recombination	\longleftrightarrow	emission
(electronic)		(optical)

Non-equilibrium Green's function theory of QPV

Microscopic model for quantum well solar cells

Tight-binding representation: basis, GF and Hamiltonian

- Basis states: **planar orbitals** = Bloch sums over transverse plane

$$|\alpha, L, \mathbf{k}_{\parallel}\rangle = \frac{1}{\sqrt{N_{\parallel}}} \sum_{\mathbf{R}_{\parallel}} e^{i\mathbf{k}_{\parallel} \cdot \mathbf{R}_{\parallel}} |\alpha, L, \mathbf{R}_{\parallel}\rangle$$

- Field operators: ($\mathbf{k} \equiv \mathbf{k}_{\parallel}$)

$$\hat{\Psi}(\mathbf{r}) = \sum_{\mathbf{k}, L} \sum_{\alpha} \langle \mathbf{r} | \alpha, L, \mathbf{k} \rangle \hat{c}_{\alpha, L, \mathbf{k}}$$

→ Green's functions, e.g.

$$G_{\alpha, L; \alpha', L'}^<(\mathbf{k}; t, t') = \frac{i}{\hbar} \left\langle \hat{c}_{\alpha', L', \mathbf{k}}^\dagger(t') \hat{c}_{\alpha, L, \mathbf{k}}(t) \right\rangle$$

→ Hamiltonian

$$H_{L, \alpha; L', \alpha'}(\mathbf{k}) \equiv \langle \alpha, L, \mathbf{k} | \hat{\mathcal{H}} | \alpha', L', \mathbf{k} \rangle$$

(Lake et al., J. Appl. Phys., **81**, 7845 (1997))

Non-equilibrium Green's function theory of QPV

Microscopic model for quantum well solar cells

Tight-binding representation: optical matrix elements

- Electron-photon interaction Hamiltonian in POB

$$\hat{\mathcal{H}}_{e\gamma}(t) = \sum_{L,L'} \sum_{\alpha,\alpha'} \sum_{\mathbf{k},\mathbf{q},\lambda} M_{\alpha,L;\alpha',L'}^{\gamma}(\mathbf{k},\mathbf{q},\lambda) \hat{c}_{\alpha,L,\mathbf{k}}^{\dagger}(t) \hat{c}_{\alpha',L',\mathbf{k}}(t) \left[\hat{b}_{\lambda,\mathbf{q}} e^{-i\omega_{\mathbf{q}} t} + \hat{b}_{\lambda,-\mathbf{q}}^{\dagger} e^{i\omega_{\mathbf{q}} t} \right]$$

- Coupling matrix elements

$$M_{\alpha,L;\alpha',L'}^{\gamma}(\mathbf{k},\mathbf{q},\lambda) \equiv -\frac{e}{m_0} \mathbf{A}_0(\mathbf{q},\lambda) \cdot \mathbf{p}_{\alpha,L;\alpha',L'}(\mathbf{k}),$$

$$\mathbf{p}_{\alpha,L;\alpha',L'}(\mathbf{k}) \equiv \langle \alpha, L, \mathbf{k} | \hat{\mathbf{p}} | \alpha', L', \mathbf{k} \rangle$$

$$= \frac{1}{N_{\parallel}} \sum_{\mathbf{R}_{\parallel}^L, \mathbf{R}_{\parallel}^{L'}} e^{i(\mathbf{k}' \mathbf{R}_{\parallel}^{L'} - \mathbf{k} \mathbf{R}_{\parallel}^L)} \langle \alpha, L, \mathbf{R}_{\parallel}^L | \hat{\mathbf{p}} | \alpha', L', \mathbf{R}_{\parallel}^{L'} \rangle,$$

$$\langle \alpha, L, \mathbf{R}_{\parallel}^L | \hat{\mathbf{p}} | \alpha', L', \mathbf{R}_{\parallel}^{L'} \rangle = \frac{m_0}{i\hbar} \langle \alpha, L, \mathbf{R}_{\parallel}^L | [\hat{\mathbf{r}}, \hat{\mathcal{H}}_0] | \alpha', L', \mathbf{R}_{\parallel}^{L'} \rangle = \frac{im_0}{\hbar} (\mathbf{R}^{L'} - \mathbf{R}^L) [H_0]_{\alpha,L;\alpha',L'}$$

(Graf & Vogl, Phys. Rev. B **51** (1995), 4940; Lew Yan Voon & Ram-Mohan, Phys. Rev. B **47** (1993), 15500)

Non-equilibrium Green's function theory of QPV

Microscopic model for quantum well solar cells

Tight-binding representation: Electron-photon self-energy

- electron-photon self-energy (Fock term of SCBA)

$$\Sigma_{e\gamma}^{\lessgtr}(\mathbf{k}; E) = i\hbar \sum_{\lambda, \mathbf{q}} \mathbf{M}^\gamma(\mathbf{k}, \mathbf{q}, \lambda) \left\{ \int \frac{dE'}{2\pi\hbar} D_\lambda^{\lessgtr}(\mathbf{q}, E') \mathbf{G}^{\lessgtr}(\mathbf{k}; E - E') \right\} \mathbf{M}^\gamma(\mathbf{k}, -\mathbf{q}, \lambda)$$

- for equilibrium propagator (optical isotropy)

$$D_\lambda^{0\lessgtr}(\mathbf{q}, E) = -2\pi i \left[N_{\lambda, \mathbf{q}}^0 \delta(E \mp \hbar\omega_{\mathbf{q}}) + (N_{\lambda, -\mathbf{q}}^0 + 1) \delta(E \pm \hbar\omega_{\mathbf{q}}) \right]$$

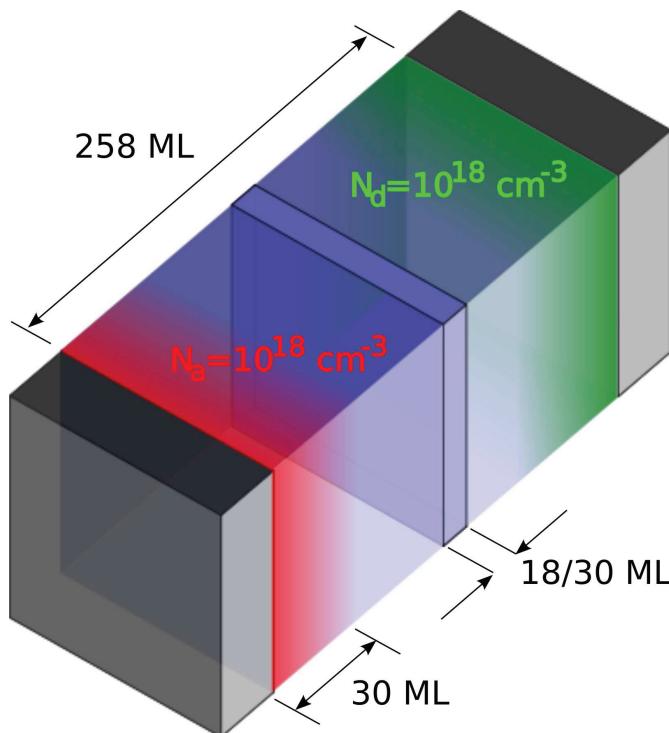
→ continuum limit

$$\begin{aligned} \Sigma_{e\gamma}^{\lessgtr}(\mathbf{k}; E) &= \frac{V}{(2\pi\hbar c)^3} \sum_{\lambda} \int d\Omega \int dE_\gamma E_\gamma^2 \mathbf{M}^\gamma(\mathbf{k}, E_\gamma, \Omega, \lambda) \left[N_\gamma^\lambda(E_\gamma, \Omega) \mathbf{G}^{\lessgtr}(\mathbf{k}; E \mp E_\gamma) \right. \\ &\quad \left. + (N_\gamma^\lambda(E_\gamma, \Omega) + 1) \mathbf{G}^{\lessgtr}(\mathbf{k}; E \pm E_\gamma) \right] \mathbf{M}^\gamma(\mathbf{k}, E_\gamma, \Omega, \lambda), \end{aligned}$$

$N_\gamma^\lambda(E_\gamma, \Omega)$: **excitation spectrum** (angle resolved)

Single quantum well photodiode

Model system



geometry:

- short active device region ~ 70 nm
- 30 ML doping $N_{d,a} = 10^{18} \text{ cm}^{-3}$
- 18 ML quantum well

material parameters:

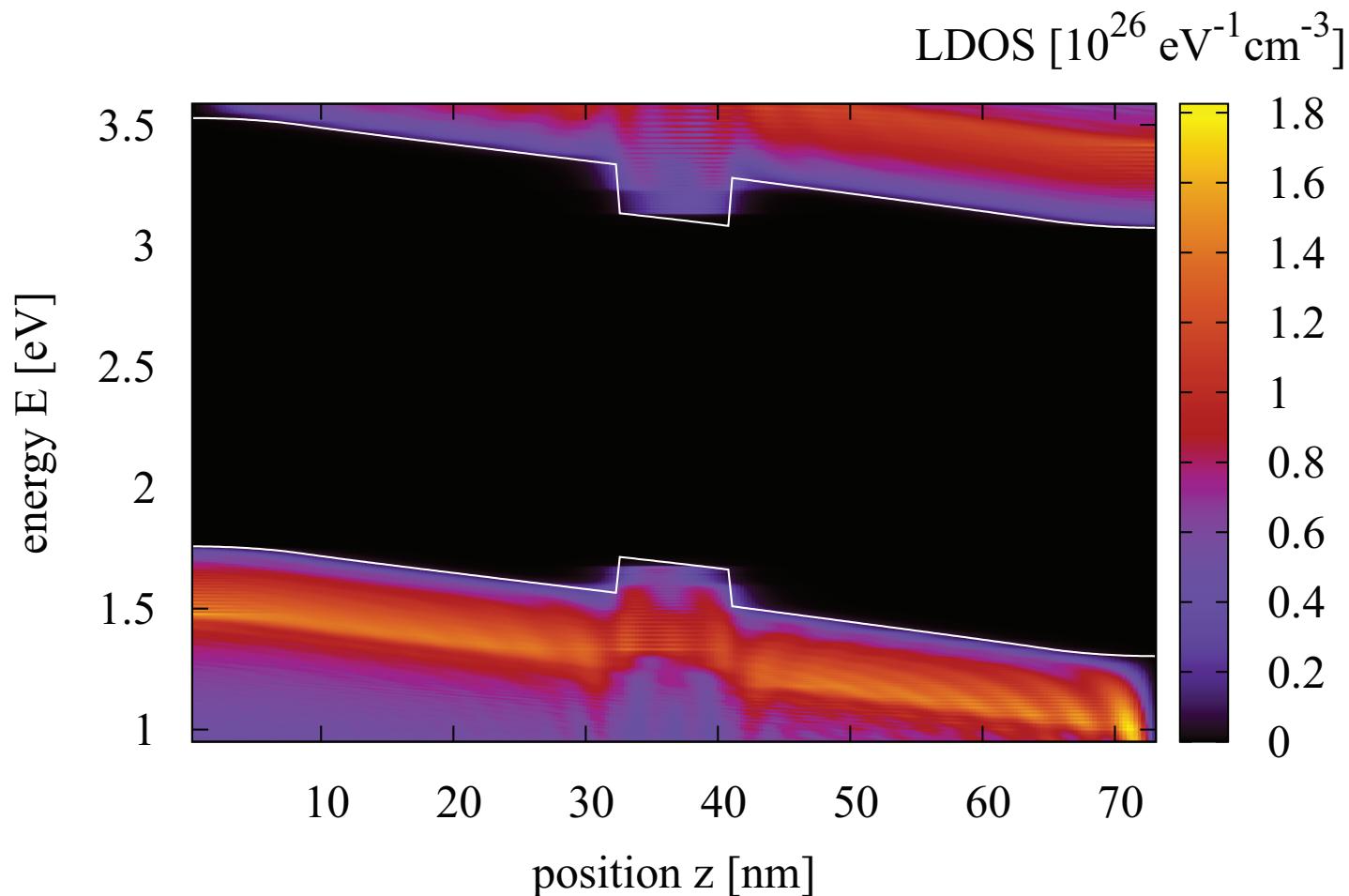
- two-band tight-binding model
- $E_{g,high} = 1.77 \text{ eV}$, $E_{g,low} = 1.42 \text{ eV}$,
 $\Delta E_C = 0.2 \text{ eV}$, $\Delta E_V = 0.15 \text{ eV}$

interaction parameters:

- monochromatic illumination
- radiative limit
- equilibrium POP- and AC-phonons
- SCBA self-energy
- coupling constants for
 $\text{GaAs-Al}_{0.3}\text{Ga}_{0.7}\text{As}$

Single quantum well photodiode

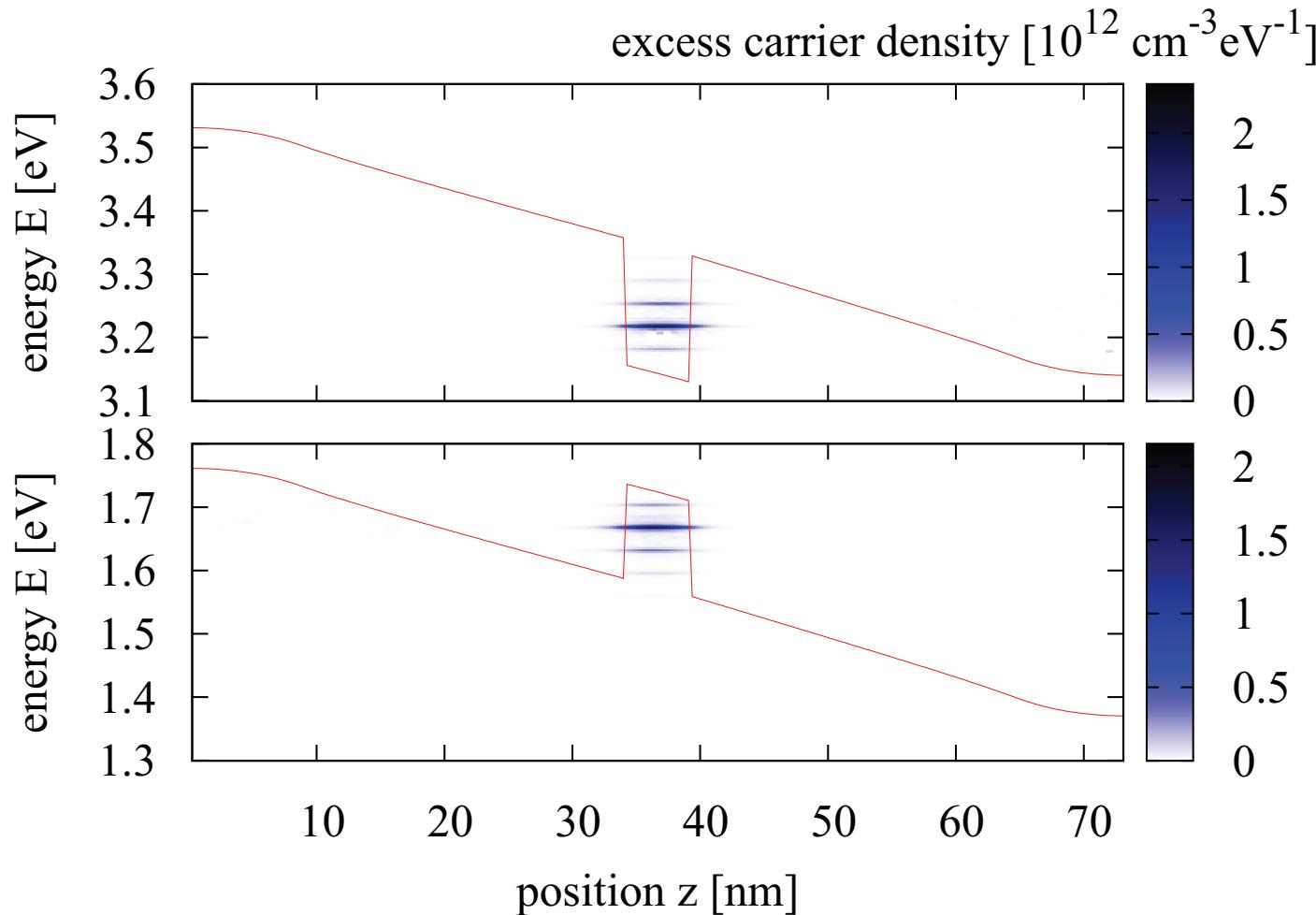
Local density of states



18 ML QW, $V_{bias} = 1.3$ V, $E_{phot} = 1.55$ eV, $I_{phot} = 17.7$ kW/m²

Single quantum well photodiode

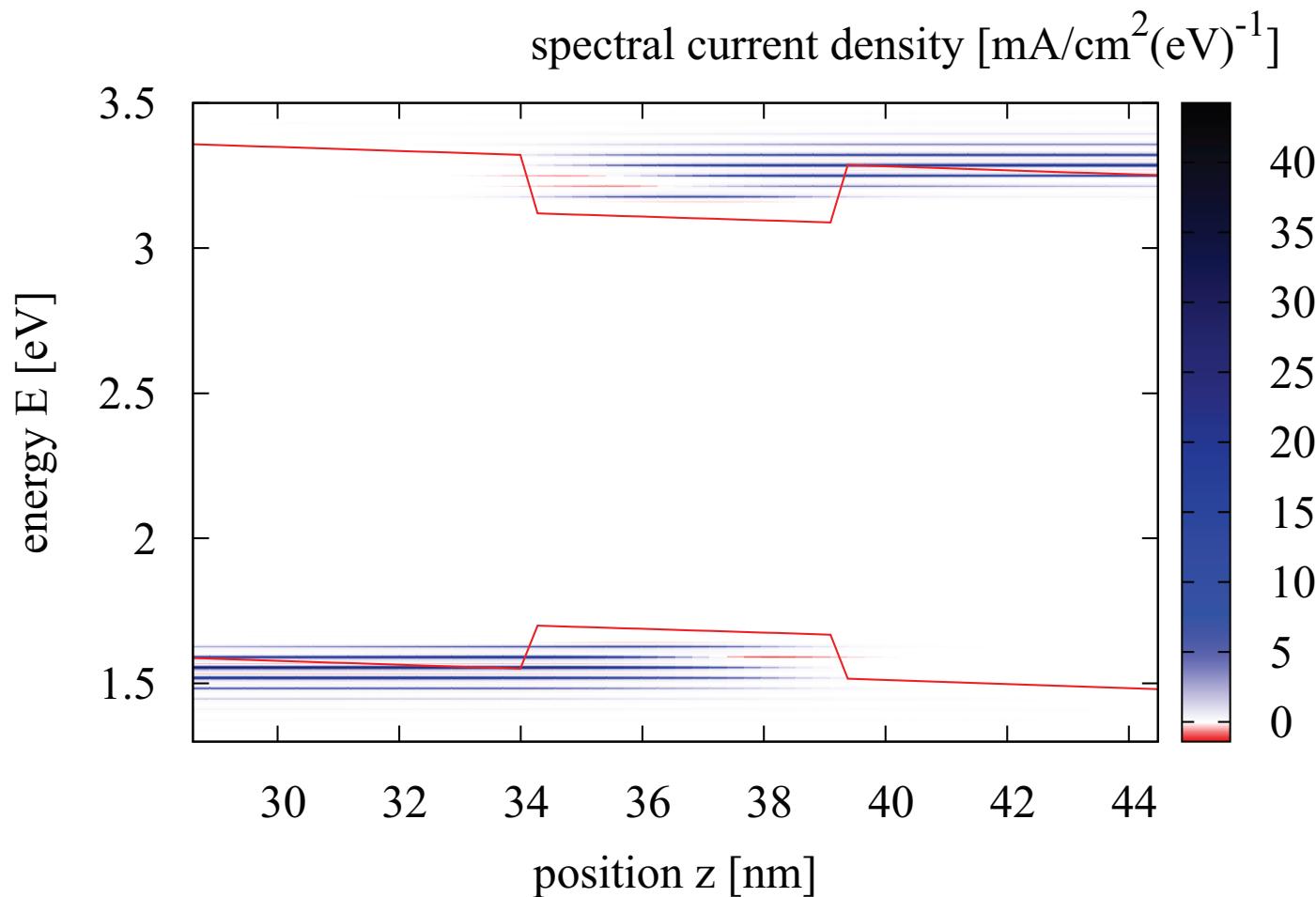
Spectral density of excess carriers



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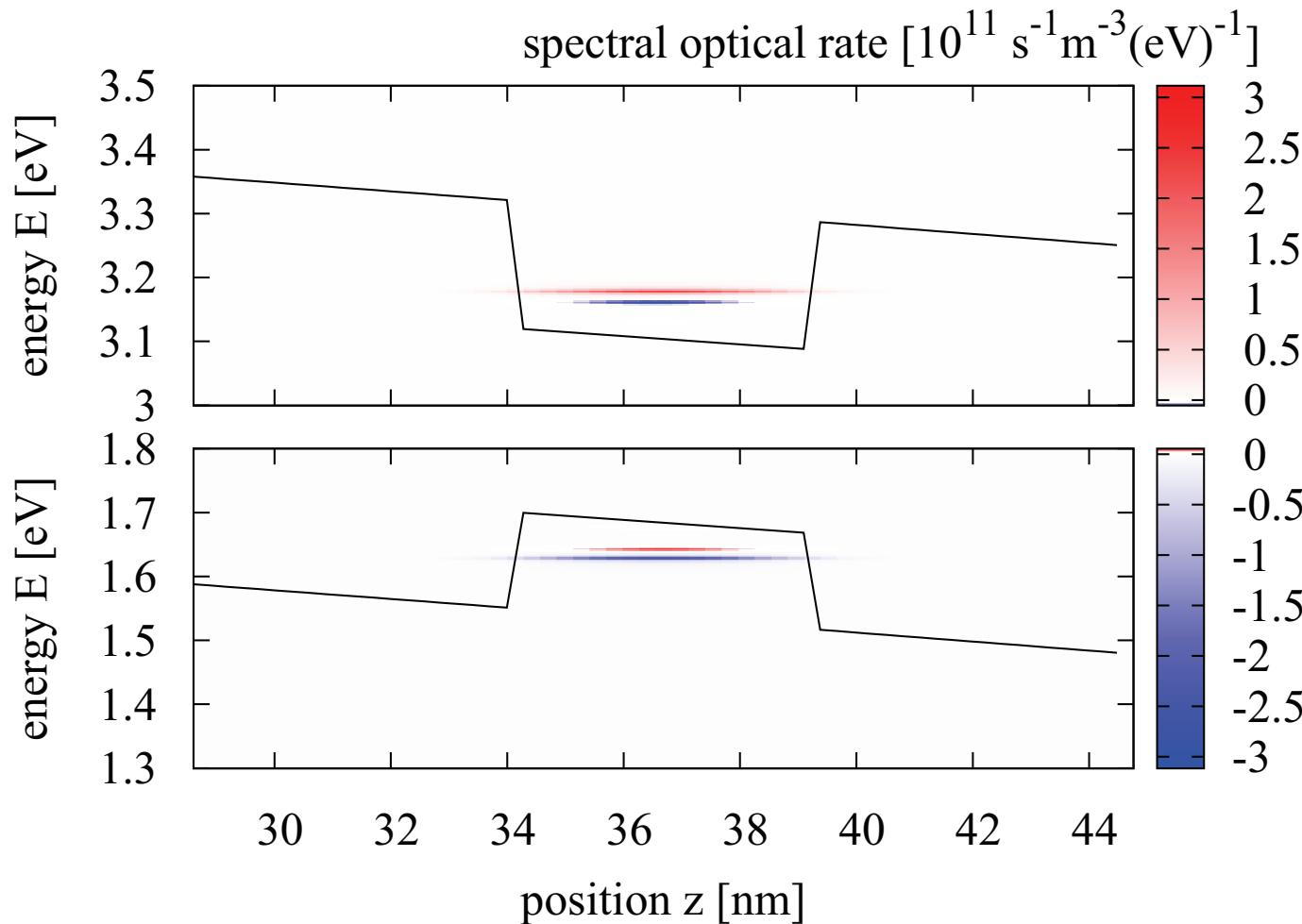
Current spectrum



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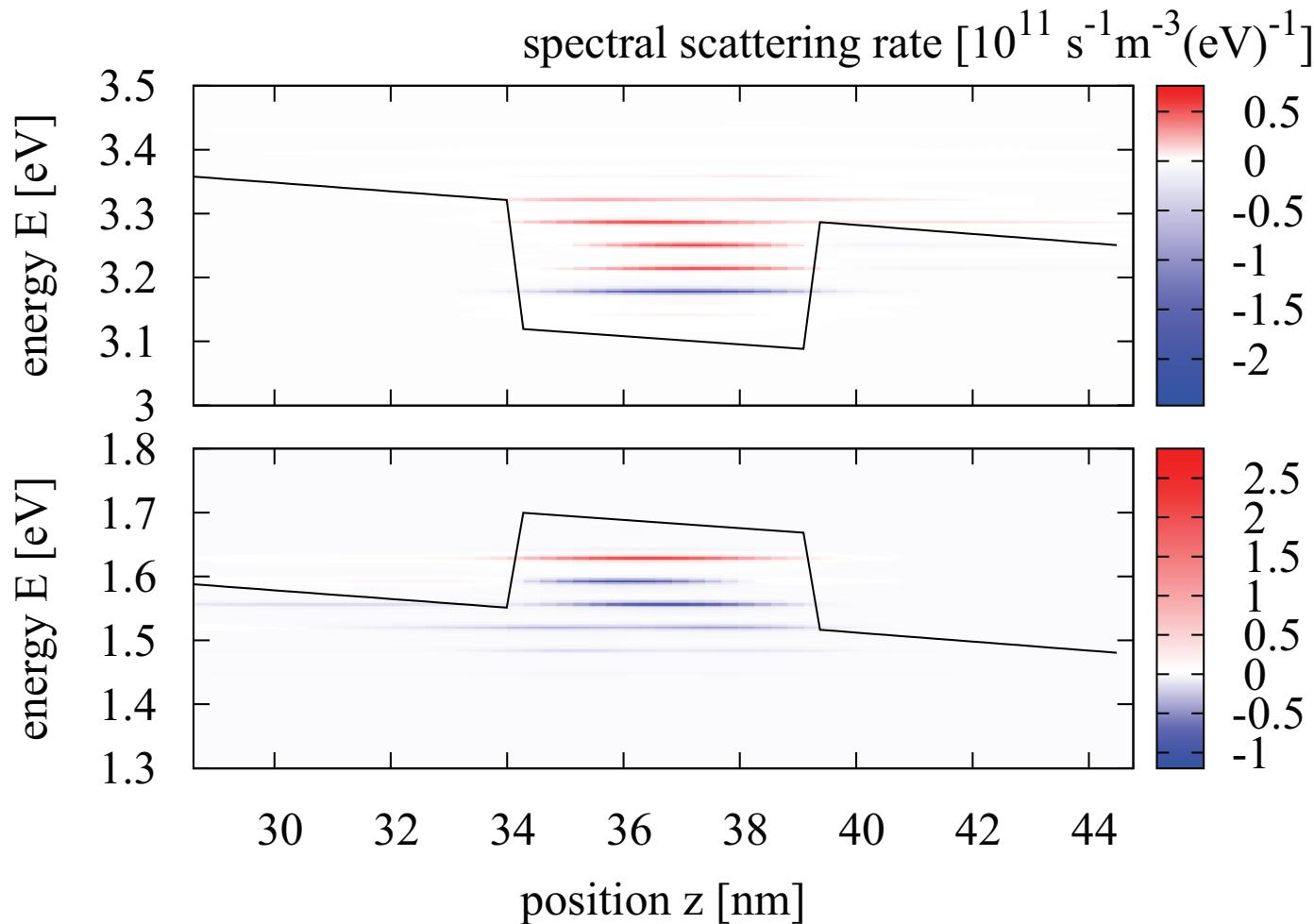
Photon scattering rate



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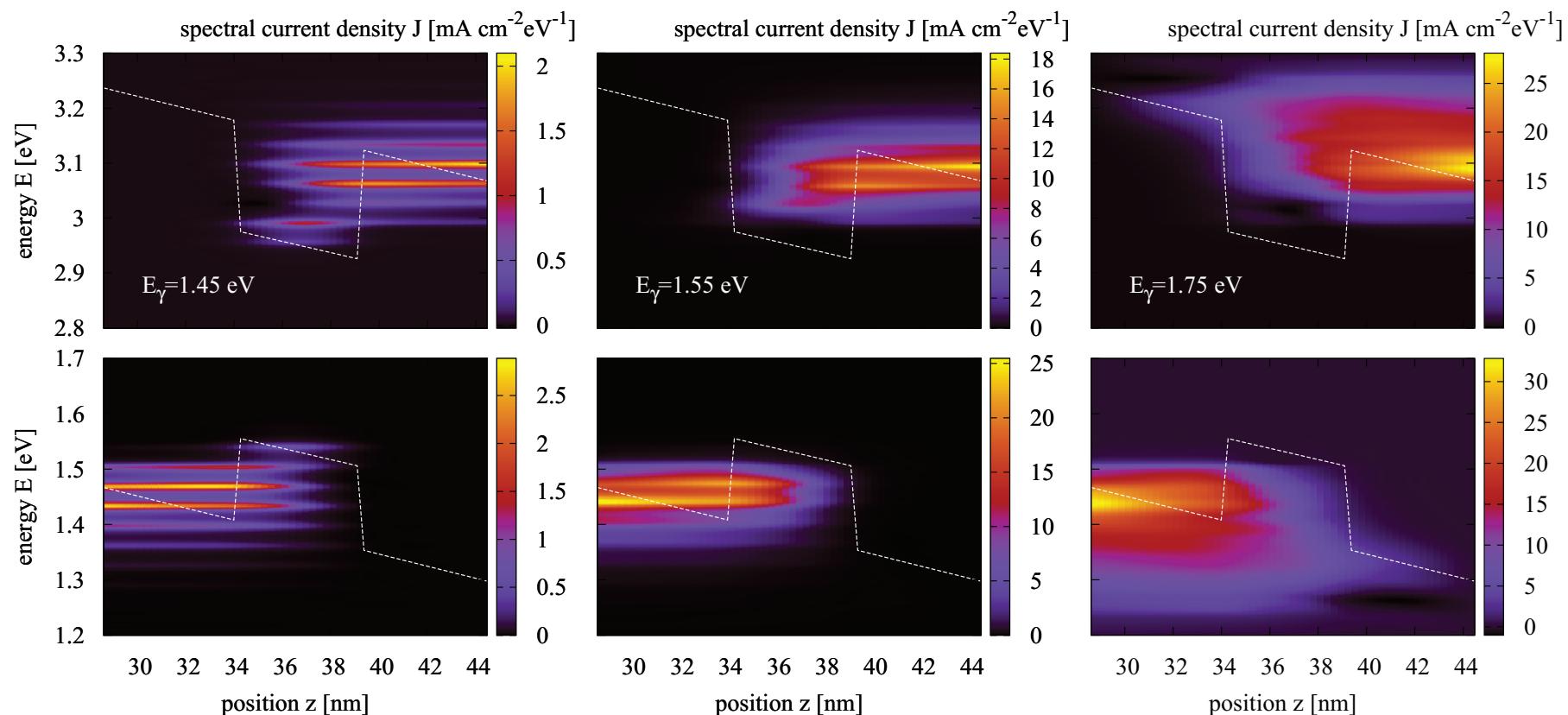
Phonon scattering rate



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Single quantum well photodiode

Excitation dependence



18 ML QW, $V_{bias} = 1$ V, $I_{phot} = 17.7$ kW/m 2

Summary & Outlook

Quantum photovoltaic devices:

- low-dimensional states & quantum effects → modified optical and transport properties
- consistent unified description: quantum kinetic theory + electronic structure calculation methods (e.g. TB-NEGF)
- valid for almost arbitrary operating conditions (high fields, high injection, . . .)
- same (realistic) electronic structure for optical excitation and transport
- Perspectives: Theory & Simulation
 - carriers: excitons, plasmons, non-radiative recombination, defects
 - photons: photon recycling, multi-photon processes, subband transitions
 - phonons: confined modes, non-equilibrium (→ hot carriers)
- first-principle methods for electronic, phononic and photonic structure
- parallel implementation and use of supercomputing resources