Rigorous simulation of photon recycling effects in perovskite solar cells and LEDs

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***Abstract*—Secondary photogeneration due to reabsorption of internally emitted photons in metal halide perovskites is assessed using a novel dipole emission model that is compatible with detailed balance rates. The model considers the non-uniform local photon density of states of thin film absorbers/emitters consistently in internal and external emission and provides insight into the impact of photon confinement on the effectiveness of photon recycling in the wave optics regime. New and general expressions for local radiative recombination and generation rates in terms of the local values of refractive index, extinction coefficient, density of states, and quasi-Fermi level splitting allow for a seamless integration of photon recycling into full opto-electronic device simulation frameworks.**

I. Introduction

In the last decade, metal-halide perovskites have emerged as a class of materials that can be used to engineer efficient and versatile solar cells and light-emitting devices [1]. In high quality metal-halide perovskite solar cells, strong optical absorption with sharp onset together with low non-radiative recombination rates leads to the presence of sizable photon recycling (PR) effects, such as increased open circuit voltage (V_{OC}) [2]. On the other hand, PR holds the potential to improve light extraction from perovskite LEDs due to redistribution of light from guided into out-coupled modes [3].

The effects of PR on the V_{OC} of perovskite solar cells were investigated theoretically in [2], [4] and the impact of photon management on PR - by different light trapping schemes - and the effects of parasitic absorption were assessed in [2], [4] by consideration of the relation between internal and external emission. While external emission is modelled in all cases based on the (angular) absorptance using the generalized Kirchhoff law [5], the evaluation of internal emission ranges from the integration of the standard van Roosbroeck-Shockley (VRS) [6] rate for radiative recombination into free-field modes [2] to rigorous simulation of dipole emission into slab modes [4]. In the former case, optical confinement effects are neglected, and the latter approaches were either restricted to single wavelength and/or suffer from the well-known issues with divergent power dissipation in dipole emission models. Also, no attempt was made so far to connect the local emission into a non-uniform local density of photon states (LDOS) to the local recombination rate entering the opto-electronic device simulation models required to assess and predict the performance of realistic solar cells.

In our contribution, we present a theory that unifies dipole emission with radiative rates from detailed balance. Consideration of the proper photon states coupling to spontaneous emission provides a numerical treatment of emission into absorbing media that is free of non-physical divergencies. The approach enables the consistent evaluation of internal and external emission under correct consideration of the photon LDOS, and allows for the determination of the secondary photogeneration rate (photon recycling) due to internal emission in a full wave picture. Furthermore, it paves the way to the rigorous propagation of PR effects from purely optical considerations to actual modifications of the electrical device characteristics as obtained from full opto-electronic device simulation.

II. Approach

The theoretical formalism on which the modelling approach is based merges the theory of dipole emission in semiconductor multilayers [7] with a local quasi-equilibrium approximation of the non-equilibrium Green's function (NEGF) framework for the quantum kinetics of excited semiconductors, which was shown to provide a consistent theory of absorption and emission in solar cells at the subwavelength regime [8]. This provides an expression of the Poynting vector as a function of the local optical material constants (refractive index n_{r} and extinction coefficient κ), the local quasi-Fermi level splitting (QFLS) $\Delta\mu_{\mathrm{cv}}$ and the dyadic Green's function $\overleftrightarrow{G}$ of the transverse fields, e.g. for the TE component:

$$\begin{aligned} S_z^y(z,E_\gamma) = &\frac{4E_\gamma^3}{\hbar^3 c_0^2\pi}\int \mathrm{d}z'\Big\{n_{\mathrm{r}}(z',E_\gamma)\kappa(z',E_\gamma)\\ &\times f_{\mathrm{BE}}\big(E_\gamma-\Delta\mu_{\mathrm{cv}}(z')\big)\Im\int\frac{\mathrm{d}^2q_\parallel}{(2\pi)^2}\Big(G_{yy}(\mathbf{q}_\parallel,z,z',E_\gamma)\\ &\times\big[\partial_z G_{yy}(\mathbf{q}_\parallel,z,z',E_\gamma)\big]^*\Big\} \end{aligned} \tag{1}$$

where z is the perpendicular position, E_γ the photon energy, $q_\parallel$ denotes the in-plane photon momentum and f_{BE} is the Bose-Einstein distribution function. While this expression provides the external emission, the internal emission is given by a generalization of the VRS relation to arbitrary photon LDOS:

$$\begin{aligned} \mathcal{R}_{\mathrm{em}}(z,\omega) = &\frac{4\omega^2}{c_0^2\pi\hbar}n_{\mathrm{r}}(z,\omega)\kappa(z,\omega)f_{\mathrm{BE}}\big[\hbar\omega-\Delta\mu_{\mathrm{cv}}(z)\big]\\ &\times\Im\big[\mathrm{Tr}\overleftrightarrow{G}(z,z,\omega)\big]. \end{aligned} \tag{2}$$

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Together with an expression for the absorptance as a function of the photon GF – which is shown to yield results in perfect agreement with the standard transfer matrix method – the two relations allow for the rigorous assessment of the generalized Kirchhoff law and evaluation of the V_{OC} enhancement due to PR at the radiative limit. The expression for the local re-absorption rate obtained from NEGF can also be derived from the rate of power dissipation in an absorbing medium, as given by classical electrodynamics in terms of the imaginary part of the dielectric function $\Im\varepsilon = 2n_{\mathrm{r}}\kappa$ and the electric field. Inserting the GF based dipole fields with detailed-balance parametrization of the dipole current source provides the generation rate due to re-absorption as follows:

$$\begin{aligned}\mathcal{R}_{\text{reabs}}(z,E_\gamma) =& \frac{8E_\gamma^4}{\pi\hbar^5 c_0^4} n_{\mathrm{r}}(z,E_\gamma)\kappa(z,E_\gamma)\int \mathrm{d}z'\Big\{n_{\mathrm{r}}(z',E_\gamma)\\ &\times\kappa(z',E_\gamma) f_{\mathrm{BE}}[E_\gamma-\Delta\mu_{\mathrm{cv}}(z')]\\ &\times\sum_{\mu,\nu}\int\frac{\mathrm{d}^2q_\parallel}{(2\pi)^2}|G_{\mu\nu}(\mathbf{q}_\parallel,z,z',E_\gamma)|^2\Big\}. \quad (3)\end{aligned}$$

The explicit expressions of the emission and reabsorption rates allow for a straightforward implementation of corresponding recombination and generation terms in an opto-electronic device simulation code, such as the Setfos tool developed by Fluxim [9].

III. Results

Figure 1(a) shows the local emission rate based on the detailed balance GF model in a methylammonium lead iodide (MAPI) perovskite slab of thickness ranging from 100 nm to 1000 nm, subject to a uniform QFLS of 1.1 eV and integrated over the photon energies 1.5< E_γ <1.85 eV. Use of the non-regularized GF (with finite momentum cutoff) overestimates the emission. The evolution of the of the V_{OC} enhancement with absorber layer thickness as obtained from the ratio of external and internal emission is shown in Fig. 1(b) for both the standard VRS rate of internal emission and the generalized rate given here. While the general trend and the oscillations due to Fabry-Pérot resonances are the same for the two models, the uniform LDOS VRS rate clearly overestimates the effect of PR at low absorber thicknesses. As could be inferred already from Fig. 1(a), the two pictures converge in the ray optics limit at large absorber thicknesses.

IV. Conclusions

We show the formal derivation and numerical implementation of a novel approach to model the impact of non-uniform density of electromagnetic modes in thin film photovoltaic absorbers and LEDs that rigorously includes the effects of photon recycling beyond the ray-optical picture. The explicit formulation of local rates in dependence of the local quasi-Fermi level splitting prepares the ground for seamless integration with opto-electronic device simulation that propagates photon-recycling effects from optical estimates to modification of the actual device characteristics of realistic perovskite solar cell and LED architectures.

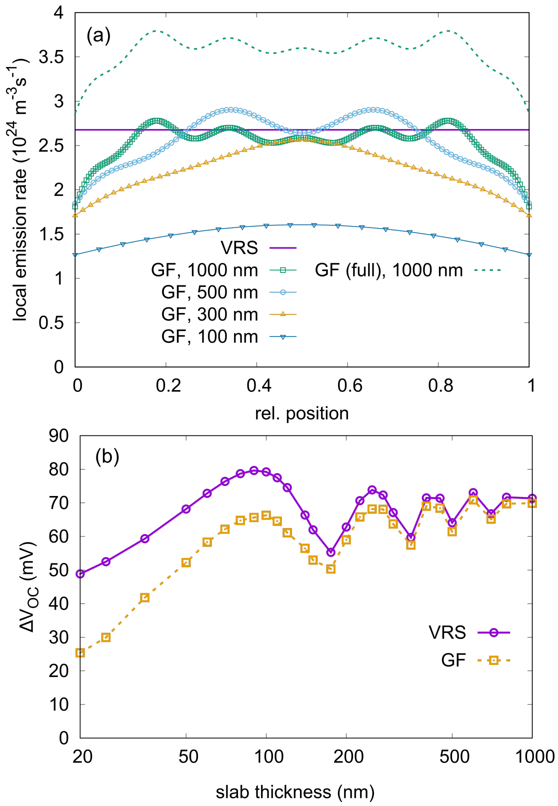

Fig. 1. (a) Local emission rate in a MAPI slab of different thicknesses, as compared to the spatially uniform VRS rate. (b) V_{OC} enhancement due to PR as a function of slab thickness, again compared to the result inferred from the VRS rate [10].

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