First-principles computation of charge-carrier recombination coefficients in optoelectronic materials

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***Abstract*-Charge-carrier recombination plays a decisive role in determining the efficiency of optoelectronic materials and devices, but their accurate experimental measurements and interpretation are challenging. In this context, first-principles computation of charge-carrier recombination coefficients is particularly useful. It allows not only rigorous computation of the recombination rates, but also intuitive interpretation of the microscopic recombination mechanisms from the electronic structure point of view. In recent years, we have developed a full set of first-principles approaches to compute the coefficients of different types of recombination processes. These methods are applied to technologically very important optoelectronic materials such as halide perovskites, which yield critical insights into the loss mechanisms and potential strategies for improved materials design.**

I. Introduction

Charge-carrier recombination is the central process that realizes energy conversion in optoelectronic materials. As schematically shown in Fig. 1, there exist first-order defect-assisted Shockley-Read-Hall (SRH) recombination, second-order radiative recombination, and third-order Auger recombination. For the SRH recombination, electron and hole recombine via a deep defect level in the band gap, which emits phonons; i.e., the energy gets dissipated in the form of heat. In radiative recombination, electron and hole directly recombine, emitting photons, which is the key light emission process for light-emitting diodes (LEDs). Auger recombination involves three carriers: two electrons and a hole (labeled eeh process) or two holes and an electron (labeled hhe process). An electron and a hole recombine across the gap, and the excess energy and momentum get captured by a third carrier (an electron or a hole), which transitions to another state higher in energy. Depending on whether phonons are involved in this process no not, Auger recombination can be characterized as a direct (no phonons) or indirect (phonon-assisted) type. Since Auger is a third-order process, it impacts the device efficiency substantially when the carrier density is high, for instance, in the case of LEDs. It may cause the well-known efficiency droop in LEDs at high injection densities [1].

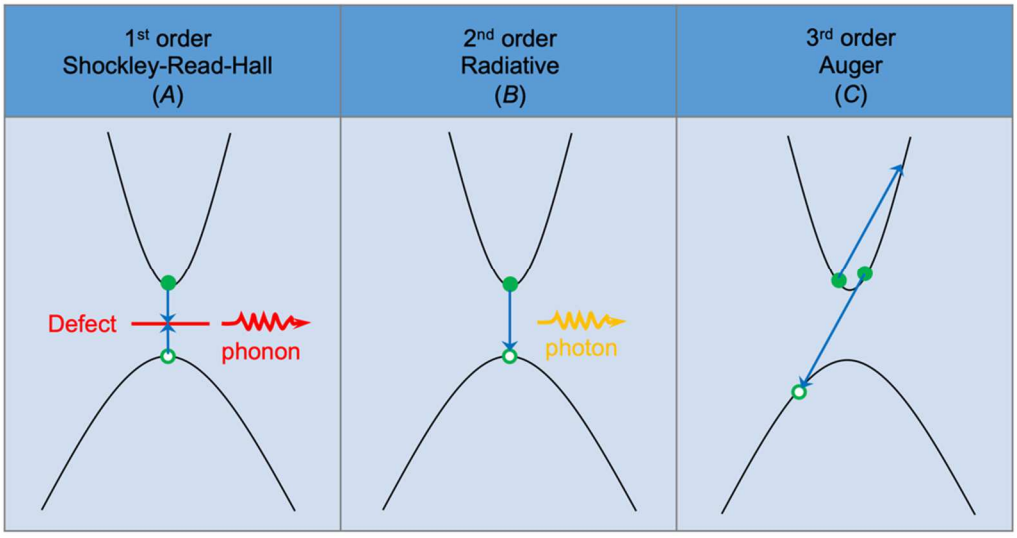

Fig. 1 Schematic for charge-carrier recombination processes of different orders.

Using LEDs as an example, its internal quantum efficiency (η) can be evaluated by

$$\eta = \frac{Bn^2}{An + Bn^2 + Cn^3}$$

where A, B, and C are the SRH, radiative, and Auger recombination coefficients, respectively. n is the carrier density (here electron and hole densities are assumed equal). Apparently, accurate determination of the recombination coefficients is key to understand and further improve the performance of optoelectronic devices, which is the primary focus of this work.

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II. Methodology

The recombination coefficients can be experimentally measured by using the carrier rate equation to fit the decay of, for instance, photoconductivity with different excitation pulse fluences. However, numerical fits of multiple parameters may involve significant uncertainties. Also, measurements of the coefficients do not allow direct and intuitive interpretation of the microscopic recombination mechanisms.

First-principles approaches may overcome this limitation, not only enable accurate computation of the recombination coefficients, but also allow direct insights into the fundamental electronic origin. In recent years, we have developed a systematic set of computational approaches to calculate the carrier recombination coefficients entirely from first principles. The key is to compute accurate electronic structure, wavefunctions, point defects, and electron-phonon coupling, which can be used to further evaluate different matrix elements. The accurate recombination rates can thus be derived by using Fermi's golden rule. More methodological details are referred to previous publications: Ref. [2], [3] for SRH, Ref. [4] for radiative, and Ref. [5] for Auger.

III. Critical Mechanistic Insights

Halide perovskites are highly efficient optoelectronic materials; the power conversion efficiency of perovskite solar cells has been approaching the efficiency record of single-crystal Si cells. They are also actively considered for LEDs, lasers, and many other applications. As compared to Si and other conventional optoelectronic materials, halide perovskites can be more easily and more cheaply fabricated, while still exhibit comparable or even better device performance.

Enormous efforts have been devoted to understand why halide perovskites are so efficient, in particular, why the carrier lifetime in halide perovskites is long, despite the fact that the material quality of halide perovskites should be poor as a result of the use of simple deposition techniques (i.e., defect concentrations are expected to be large). However, lots of controversial mechanisms have been reported in the literature.

By applying our rigorous methodology to halide perovskites, we have uncovered many interesting and important insights into the microscopic carrier recombination mechanisms in halide perovskites, and resolved many controversies.

For SRH recombination, we identified iodine interstitials [6]–[8] and hydrogen vacancies [9] as efficiency-killing recombination centers. We clearly demonstrated that the commonly believed "defect tolerance" of halide perovskites is misguided [10].

For radiative recombination, we found that the Rashba spin [11] and momentum [4] splitting has a minor impact on the radiative coefficient, in clear contrast to many experimental and theoretical reports in the literature.

In terms of Auger recombination, we showed that the Auger coefficients in halide perovskites are unexpectedly strong due to some resonance in the band structure [12], and can be suppressed by alloying [13].

IV. Summary

Charge-carrier recombination coefficients can be accurately computed from our recently developed first-principles approaches, which also allow to derive the underlying mechanisms and effective strategies to engineer the recombination coefficients. These approaches are computationally efficient and generally applicable to a large variety of optoelectronic materials, which will assist the computational design of highly efficient optoelectronic materials.

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