Perspective

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Quantum Dynamics of Photogenerated Charge Carriers in Hybrid Perovskites: Dopants, Grain Boundaries, Electric Order and Other Realistic Aspects

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ABSTRACT: Dissipation of photon energy to heat and recombination of photogenerated charge carriers are among the main factors limiting the efficiency of solar-light harvesting devices. The dynamics of excited electrons and holes depend critically on the microscopic structure of a material, including dopants, defects, grain boundaries, crystallinity and electric order. The perspective summarizes recent findings and suggests directions for improvement of hybrid organic-inorganic perovskite materials, established by means of non-adiabatic dynamics (NAMD) simulations. Combined with real-time time-dependent density functional theory, NAMD provides an \textit{ab initio} description of the photo-initiated processes that occur far from thermodynamic equilibrium. It includes realistic aspects of material’s structure and gives unique atomistic insights into the photo-active material properties.
Because of their outstanding optical and electronic properties on the one hand, and low production costs on the other, hybrid organic-inorganic perovskites (HOIP) have been recognized as highly promising materials for photovoltaic applications\textsuperscript{1–6}. Intense research efforts led to an unprecedented progress in the perovskite solar cells efficiency, recently reported to exceed 22\%\textsuperscript{7}. From the materials science perspective, photogenerated charge losses due to electron-hole recombination are among the major factors setting limits upon this value. The unwanted charge recombination may be realized through different mechanisms,\textsuperscript{8–12} including non-radiative, radiative, trap-assisted and Auger-assisted recombinations. The two-body non-radiative charge recombination occurs even in high quality, defect-free materials exposed to moderate-to-high illumination. Often, the recombination occurs on sub-nanosecond timescales, inevitably competing with charge carrier diffusion within the active medium towards the electron and hole transporting layers and, thus, reducing the charge extraction efficiency.

Experimental lifetimes of electrons and holes in hybrid perovskites range from several nanoseconds to microseconds, depending on numerous material- and environment-related factors\textsuperscript{5,13–17}. Here, we overview recent theoretical studies concerning charge relaxation and recombination in hybrid perovskites, performed with non-adiabatic molecular dynamics (NAMD) and steady-state Fermi-golden-rule approach. The discussion focuses on realistic aspects of HOIP geometric and electronic structure, and includes hot carrier cooling, photo-induced charge transfer between perovskite and electron-accepting material, doping and grain-boundary effects, consequences of material exposure to moisture, influence of electric order, and modification of the electronic structure near the bandgap edges by spin-orbit coupling. All these phenomena are ubiquitous in HOIP materials, constantly affecting their photovoltaics properties. At the same time, their individual contributions are hard to extract from the experimental data. For that, quantum dynamics simulations constitute a unique and extremely valuable tool to study the exact mechanisms of energy loss and charge recombination, significantly advancing our fundamental understanding of these processes.

**Non-adiabatic molecular dynamics generates time-domain atomistic insights into far-from-equilibrium evolution of electrons and nuclei**

Mixed quantum-classical methodologies provide an affordable and sufficiently accurate approach to real-time dynamic simulations of chemical and physical processes in condensed
phases. Within the quantum-classical picture the nuclear degrees of freedom are treated classically and follow the Newton equation of motion, while the quantum electronic subsystem evolves by the time-dependent Schrödinger equation (TDSE). Typically, the electronic wave function, \( \Psi(t, \vec{r}^{3N}) \), is expressed in the basis set of all possible electronic adiabatic states, \( \psi(\vec{r}^{3N}; \vec{R}^{3N}(t)) \),

\[
\Psi(t, \vec{r}^{3N}) = \sum_k c_k(t) \psi_k(\vec{r}^{3N}; \vec{R}^{3N}(t))
\]

where \( \vec{r}^{3n} \) and \( \vec{R}^{3N} \) are the coordinates of \( n \) electrons and \( N \) nuclei. With subsequent insertion of the expanded wave function into the TDSE, one arrives at time-evolution relation for the electronic wave function expansion coefficients

\[
i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_k c_k(t) (\epsilon_k \delta_{jk} + d_{jk})
\]

where \( \epsilon_k \) is the energy of the adiabatic state \( k \), and \( d_{jk} \) is the non-adiabatic coupling between states \( k \) and \( j \). The non-adiabatic coupling is created by atomic motions and reflects the strength of electronic response to nuclear vibrations. \( d_{jk} \) can be calculated numerically as an overlap of orbitals \( j \) and \( k \) at sequential dynamics time steps:

\[
d_{jk} = -i\hbar \langle \psi_j | \nabla_{\vec{R}^{3N}} | \psi_k \rangle \cdot \frac{d\vec{R}^{3N}}{dt} = -i\hbar \langle \psi_j | \frac{\partial}{\partial t} | \psi_k \rangle
\]

In the surface hoping realization of non-adiabatic dynamics, the system undergoes transitions (hops) between electronic states. A variety of surface hopping algorithms have been developed to address particular types of systems and processes. The calculated evolution is typically averaged over a large number of classical nuclear trajectories and surface-hopping stochastic realizations to give high quality time-dependent picture of the systems dynamics.
In the following sections of the Perspective we discuss several case-studies covering different realistic aspects of the photodynamics in hybrid perovskites in the context of their photovoltaic performance.

**Halide mixing can slow down hot-carrier intraband relaxation.**

In order to maximize power extraction from a solar cell, one needs to capture and transform into electric energy as much of the incident energy carried by absorbed photons as possible. On the one hand, this means that the active-material bandgap should match the near infrared light frequencies corresponding to the lower bound of the high-intensity solar spectrum reaching the Earth surface, since all higher-energy photons should be still absorbed by dense manifold of states building up the valence and conduction bands. On the other hand, the same dense structure of the bands facilitates an ultrafast excited carrier cooling to the band edges, following directly the absorption process. The relaxation results in significant energy losses and limits solar cell voltage. The power leakage could be avoided by extracting hot carriers before they cool down. Although such hot carrier collection is experimentally challenging, theoretical investigations based on time-dependent methods can guide future experimental research by providing insights into the cooling process. The issue has been recently investigated by Madjet *et al.*\(^{20}\) for a set of hybrid halide perovskites, in the wider context of the role of halogen mixing for the cooling process dynamics.

The NAMD simulations were employed to investigate the interstate non-adiabatic coupling within the valence and conduction bands to model the energy relaxation of the hot hole and hot electron. This approach allows for both direct identification of the cooling timescales and assignment of the lattice vibrational motions having most pronounced impact on the process. In the case of the reference \(\text{CH}_3\text{NH}_3\text{PbI}_3\) (MAPbI\(_3\)) system in its room-temperature stable tetragonal phase, it was found that the intraband electron cooling, depending on the initial excess of the excitation energy, occurs within 350-850 fs, which stays in line with the recent experimental findings\(^{9,11,21}\). The hot-hole relaxation is even faster than the hot-electron relaxation, and is predicted to complete during first 700 fs after the excitation for the highest 1 eV over-bandgap initial hole energy. The difference in the cooling rate for the electrons and holes is rationalized in terms of lower density of states (DOS) observed in the conduction band, in which the relaxation of hot electrons occurs. The calculations show that both cooling processes are driven mostly by
the inorganic-lattice vibrations, with certain effects arising from the lattice coupling with the organic-moiety modes. The importance of the organic subsystem has been established recently by numerous studies as crucial for correct understanding of the hybrid perovskites electronic properties \(^{22-25}\).

The NAMD charge-cooling study demonstrated an interesting impact of halogen mixing on the carrier relaxation. This effect was modeled through 8% replacement of the iodine atoms with bromine and chlorine. As a result of the replacement, a factor of two retardation of the cooling is observed for the chlorine substitution. It is explained by a partial charge localization on the substituted atoms and the consequent decrease of the interstate non-adiabatic couplings. Such an effect, however, was not observed for bromine. Thus, in addition to the detailed understanding of the hot-carrier cooling dynamics, the discussed NAMD investigation sets up a possible direction for experimental efforts towards efficient hot carrier extraction from the hybrid perovskites materials, proposing chlorine doping as a structural modification of choice.

**Effects of dopants and interfacial interactions on charge separation and recombination.**

The interplay between dopants and host lattice often change geometric and electronic structures of parent materials and affects excited-state properties in solar cell systems. Experiment showed that non-radiative electron-hole recombination in solar cells composed of TiO\(_2\) sensitized with MAPbI\(_3\) reduces when iodides are substituted with chlorines or bromines. In contrast, the recombination increases when lead is replaced with tin.\(^{13,26-28}\) These findings are rather unexpected and would have been hard to predict *a priori*, in particular since all three dopants are lighter than the atoms they substitute, and since higher frequency vibrations introduced by lighter atoms might be expected to accelerate the recombination.

*Ab initio* NAMD simulations performed on pristine and doped MAPbI\(_3\)(100)/TiO\(_2\) anatase (001) interfaces establish the mechanisms of the energy and charge losses, and suggest practical means for controlling the interfacial electron-hole recombination.\(^{29}\) The simulations support the experimental observations that doping with Cl and Br reduces the recombination rate, while doping with Sn increases the rate, **Figure 1 a**. The established results are rationalized by a combination of three factors. First, Cl and Br decrease the MAPbI\(_3\)/TiO\(_2\) bonding interaction, while Sn increases the bonding. Second, Cl and Br diminish the donor-acceptor and non-
adiabatic coupling, while Sn enhances the coupling. Third, Cl and Br accelerate loss of quantum coherence, while Sn leaves the decoherence time largely unchanged. Similar dopant effect was also observed in the theoretical study on pristine MAPbI₃. The recombination is driven by coupling of the electronic subsystems to low-frequency bending and stretching modes of I-Pb bonds in perovskite and acoustic modes in TiO₂. The obtained time scales agree well with the time-resolved experimental data. The study characterizes the fundamental mechanisms lying behind the energy losses, such as wave function overlap and quantum coherence, and provides practical guidelines, such as specific suggestions for rational choice of dopants, for reducing charge recombination and designing higher efficiency perovskite solar cells.

Interestingly, another recent NAMD study on the photophysics at the perovskite/TiO₂ interface has uncovered that, in the presence of strong, covalent-like interaction between the perovskite and electron-accepting component, an ultrafast electron transfer may occur on a sub-100 fs timescale. The strong, finite-temperature-induced interactions facilitate number of pathways for the electron to be transferred, including direct inter-component excitation, adiabatic, and non-adiabatic mechanisms, Figure 1 b. The ultrafast interfacial injection guarantees efficient photo-induced charge separation that creates favorable conditions for operation of perovskite solar cells.

Figure 1. a. Left: Simulation cell of the MAPbI₃(100)/TiO₂ anatase (001) interface. Right: Energy level diagram. The electron-hole recombination occurs by electron transfer from the TiO₂ conduction band minimum to the perovskite valence band maximum. Replacement of I with Cl or Br reduces electron-hole recombination, while substitution of Pb with Sn accelerates this process. b. Scheme of the photoinduced electron transfer (ET) mechanism. Adiabatic ET occurs
by passing over a transition state barrier (curved red arrow). Non-adiabatic ET occurs via a hop between donor and acceptor states (downward blue arrow). Photoexcitation can promote the electron directly from the donor material to a state that is localized on the acceptor (upward green arrow), creating a charge separated state. Adapted from Ref.29 (a.) and Ref.33 (b.).

**Grain boundaries accelerate charge recombination in the CH$_3$NH$_3$PbI$_3$ perovskite.**

MAPbI$_3$ perovskites unavoidably contain grain boundaries (GBs) that affect the excited state lifetime and solar cell performance. First-principles calculations predicted that MAPbI$_3$ GBs are benign because no deep trap states are found.$^{34,35}$ However, factors other than the state energy, in particular, the NA coupling and quantum coherence time, influence the nonradiative electron-hole recombination significantly. Even though shallow defects have only a minor influence on the bandgap, they can affect strongly elastic (coherence) and inelastic (NA coupling) electron-phonon scattering. According to the energy gap law, the recombination rate is approximately linear in the energy gap. According to Fermi’s golden rule, the rate is proportional to the NA coupling squared, and depends strongly on the decoherence time, which enters the rate expression through the Franck-Condon factor. The dependence on the energy gap is weakest among the three factors, and the influence of decoherence is the subtlest. Therefore, it is hard to predict *a priori* by static electronic structure calculations whether defects accelerate charge recombination or decelerate it; to approach this problem thoroughly, one requires more advanced NAMD simulations to determine directly the nonradiative decay dynamics.

Experiments contradict the static electronic structure prediction$^{34,35}$ and show that GBs notably degrade the film optoelectronic properties.$^{15,36,37}$ Tosun and co-authors demonstrated that annealing perovskite films in the presence of MAI vapor increases grain size and results in longer excited-state lifetime.$^{37}$ Bischak *et al.* reported significant differences in non-radiative recombination rates from grain to grain within MAPbI$_3$ films using cathodoluminescence microscopy.$^{36}$ Snaith and co-authors showed that the electron-hole recombination rate significantly increases in the presences of GBs, while it is reduced with Cl doping.$^{15}$

The discrepancy between the experiment and theory motivated the *ab initio* NAMD simulations focusing on electron-hole recombination in pristine MAPbI$_3$ and MAPbI$_3$ containing GB with and without Cl passivation.$^{38}$ The NAMD study demonstrated that GBs strongly
accelerate the electron-hole recombination relative to the bulk MAPbI$_3$, while introduction of substitutional Cl dopants at the boundary reduces the recombination,\textsuperscript{38,39} Figure 2. The acceleration of the charge recombination at GBs is attributed to three major effects. First, GBs introduce trap states, reducing the electron-hole energy gap and bringing the electronic and vibrational quanta closer to resonance. Second, GBs increase the non-adiabatic electron-phonon couplings between the electron and hole wave functions by localizing the wave functions at the boundary, and by creating additional phonon modes that couple to the electronic subsystem. Third, the phonon-induced decoherence time remains largely unchanged because no foreign atoms are incorporated into the lattice. Once lighter chlorines substitute heavier iodines at the GB, they introduce higher-frequency vibrations and accelerates quantum coherence loss. Further, in contrast to I, the Cl dopants do not contribute to the hole wave function, thus, eliminating some of the wave function overlap, reducing the non-adiabatic electron-phonon coupling, and restoring its value close to that for the pristine MAPbI$_3$. Both factors arising from the doping compete successfully with the reduced bandgap relative to the pristine MAPbI$_3$, and slow down the electron-hole recombination. The discussed NAMD results show excellent agreement with experiment,\textsuperscript{31,32} establishes how GBs and chlorine dopants affect electron-hole recombination in perovskite solar cells, and suggest a valuable route to increasing photon-to-electron conversion efficiency through rational GB passivation.
Figure 2. Top: Simulation cell of the MAPbI₃ grain boundary system. Bottom: Energy level diagram. The nonradiative charge recombination occurs by interaction of an electron from the conduction band minimum with a hole at the valence band maximum of the perovskite. Grain boundary accelerates the recombination, while replacing the I atoms by the Cl atoms at the grain boundary slows down it. Adapted from Ref. 38.

Moderate humidity slows down electron-hole recombination at the CH₃NH₃PbI₃ surface.

The effect of humidity on the HOIP properties can be either positive⁴⁰,⁴¹ or negative,⁴²,⁴³ having a strong impact on the solar cells performance, as reported by different experiments. On the one hand, some measurements demonstrate that humidity increases the excited-state lifetime of MAPbI₃ and improves the solar cells performance.⁴⁰ On the other hand, some experiments show that moisture accelerates the electron-hole recombination in MAPbI₃ and degrades the solar cell quality.⁴² Because halide perovskites are highly-polar salts, they are prone to dissociation in water, and the resulting structure modification affects the photovoltaic performance. Macroscopically, it has been suggested that humidity level influences crystalline grain size. However, the presence of water affects not only grain size of films, but also the electronic structure. The microscopic origin of the positive or negative impact of humidity on perovskite solar cells is unclear. In particular, the influence of relative humidity on non-radiative electron-hole recombination remains unknown.

Motivated by the experiments,⁴⁰–⁴³ ab initio NAMD simulations were performed to investigate the non-radiative electron-hole recombination at the MAPbI₃ (001) surface covered by a varying number of water molecules⁴⁴. The study indicated that exposure to small amounts of water can slow down electron-hole recombination, while large water amounts accelerate the recombination. In small quantities, water molecules perturb the surface layer and localize the photo-excited electron close to the surface, Figure 3. Importantly, the localized state does not create a deep electron trap. As a result, the electron-hole overlap decreases, and the quantum coherence time decreases as well. Both factors reduce the electron-hole recombination and increase the excited-state lifetime. In large quantities, water molecules prefer to accumulate on the MAPbI₃ surface and form stable hydrogen-bonded networks. Water molecules aggregated into a continuous film need to overcome a higher barrier to break the film and enter MAPbI₃. A
water film has little influence on charge localization, and the electron-hole overlap is not affected, compared to the bare surface, Figure 3. At the same time, the NA coupling grows in MAPbI$_3$ covered by a water film due to participation of high frequency water vibrations, and the excited state lifetime shortens. The obtained electron-hole recombination timescales show good agreement with the available experimental data.$^{31,32}$

The discussed study reveals the importance of relative humidity on the excited-state lifetime of MAPbI$_3$ perovskite, highlights the factors affecting the electron-hole recombination, and provides insights that can be used to improve the performance of perovskite solar cells. In particular, the short-range chemical and long-range electrostatic mechanisms of perovskite-water interaction are identified to provide control over charge localization and recombination. Moreover, the simulations suggest that different solvents can have different effects on the electron-hole recombination, depending on the relative strength of the solvent-solvent and solvent-perovskite interactions.

**Figure 3.** Electron-hole recombination between the conduction band minimum and valence band maximum of the perovskite depends on the relative humidity. Small amounts of water extend the exited-state lifetime, while large quantities of water molecules decrease the lifetime compared to bare perovskite. Adapted from Ref. $^{44}$. 
Local electric order inhibits non-radiative electron-hole recombination.

The outstanding photovoltaic and synthetic properties of HOIP materials stem from a beneficial combination of features of their both components. In particular, the organic component is responsible for controlling the inorganic-part dimensionality which further influences the bandgap size and exciton binding energy. Until recently the understanding of the role of electrostatic interactions between the organic and inorganic layers has been limited to recognition of their mutual structure-stabilizing effects. The experimental and theoretical results reported lately have changed this point of view dramatically, suggesting the fundamental connection of the dynamic interaction between the organic and inorganic components to such crucial photovoltaic features as material bandgap, photogenerated charge localization and electrostatic screening.

The effect of a local electric-dipole order of organic cations on the non-radiative hole-electron recombination was investigated by NAMD for a hybrid perovskite exhibiting room-temperature stable ferroelectric phase. Focusing on the (benzylammonium)\textsubscript{2}PbCl\textsubscript{4} system, Figure 4 a., chosen for its proven stable polar C-N bonds orientation, it was demonstrated that electrostatic interactions within the organic component have a significant impact on the excited state lifetime. Depending on the alignment pattern of the polar C-N groups, Figure 4 b., the non-adiabatic coupling between the band edge states of electron and hole may change its value by more than 20%, enhancing or suppressing charge recombination. Ferroelectric, ordered arrangement of polar organic groups is found to slow down bandgap energy vibrations, which can be noticed in the calculated power spectrum, Figure 4 c.. This results in the inhibition of the non-radiative electron-hole recombination. This local effect, working hand-in-hand with the field-induced long-range effects, such as electron-hole separation and improved carriers mobility leads to prolonged charge-carrier lifetimes. The slowdown of the photogenerated hole-electron recombination due to the locally ordered ferroelectric alignment is predicted at the order of ca. 20%.
Figure 4: a. Structure of stable room-temperature ferroelectric phase of (benzyl-ammonium)$_2$PbCl$_4$. Pb is grey, Cl is green, N is dark blue, C is orange, and H is turquoise. Purple arrows indicate the aligned C-N bonds responsible for the cell dipole moment. b. Top view of crystal cells chosen to model the ferroelectric (ferro) and paraelectric (anti-ferro, mixed) material phases. Black dots mark the Pb atoms positions, and polygons illustrate the network of the in-plane Cl atoms occupying the polygons corners. Polygon color marks the micro-domain polarization: purple/green is used for ferroelectric/paraelectric dipole moment alignment, respectively. Red and dark-blue arrows show the dipole moment orientation for the upper and lower organic layers. Black dashed-line squares mark the bc-plane cross-section of the unit cell. c. Power spectra (continuous solid lines) and low-energy IR vibrational spectra (vertical ticks) for ferro (black), anti-ferro (red) and mixed (green) forms. The gray ticks in the background mark frequencies of all modes calculated for a particular form. Adapted from Ref. 49.

Electron-hole recombination is slowed down by the Rashba effect.

Exceptionally long lifetimes of photogenerated charge carriers are among recognized crucial features of hybrid perovskite materials leading to their excellent photovoltaic performance. The reason for their slow charge recombination rate, usually characterized by nanosecond and longer lifetimes, has not been unequivocally determined, though. Among possible explanations one may consider ultrafast quantum decoherence suppressing the non-adiabatic dynamics of the charges,$^{29,39,45,49}$ as has been already pointed out in the previous sections. Another cause could be dynamic charge localization and screening due to rotations of
the polarized molecular cations\textsuperscript{24,45–48} or effective charge separation at the bulk ferroelectric domains walls\textsuperscript{52}. Recently another explanation for this ultra-long carriers lifetime, based on the Rashba effect, has been proposed.\textsuperscript{54–58}

In the presence of electric field, systems exhibiting strong spin-orbit coupling experience lift of the spin degeneracy within their electron bands, Figure 5 a. Known as the 3D Rashba phenomenon, the splitting leads to spin-allowed and spin-forbidden transitions in materials that contain heavy atoms and, at the same time, exhibit bulk ferroelectricity. Hybrid perovskites can satisfy these two conditions due to the presence of Pb (or I, Br) atoms that are known to show strong relativistic effects,\textsuperscript{59,60} and the possibility of domain polarization by local alignment of the organic moieties.\textsuperscript{49–53} Since the intra-band hole and electron cooling are much faster than the charge recombination, the electrons and holes recombine from the edges of the conduction and valence bands. The Rashba splitting may lead to various spin patterns at the band edges, resulting in some cases, in a mismatch between the lowest conduction and highest valence state spin orientations. Such mismatch would slow down the charge recombination stemming from low probability of spin flip. Moreover, upon the splitting, the conduction and valence band edges experience slight shifts in the k-space. The shifts change the bandgap character from direct to indirect, further retarding the recombination process, since now it requires not only energy but also momentum transfer. The exact pattern of the state spin orientations depends on the details of material structure. The direct-to-indirect bandgap transition in HOIP was recently observed in experiments,\textsuperscript{12} rationalizing the thermally enhanced, long, secondary charge recombination pathways.

It was recently reported by Zheng and co-authors\textsuperscript{54} for the MAPbI\textsubscript{3} perovskite in its typical cubic and tetragonal phases that a slight shift of the Pb atom is required for the Rashba splitting to occur and to exhibit the spin mismatch between the valence and conduction band edge states, Figure 5 b. & c.. Such distorted structures have been predicted to be thermally accessible in room-temperature conditions and to be further stabilized by the aligned molecular cations orientation. The exact charge-lifetime enhancement depends on the Rashba-induced energy splitting between the states and, for the splitting of 0.1 eV, it is expected to reach a factor of 10 as was estimated within the Fermi’s golden rule approach.\textsuperscript{54}
Figure 5. a. Diagram of Rashba bands and the electron transport path. The cyan and orange arrows show the directions of the spins. The spin texture $\chi$ indicates spin vortex direction with its signs characterizing spin rotation in “clockwise” ($\chi = -1$) and “counterclockwise” ($\chi = +1$) directions. Photo-excited electrons in conduction bands $C_{\chi=+1}$ and $C_{\chi=-1}$ quickly relax to the $C_{\chi=-1}$ band minimum due to the inelastic electron-phonon scattering. Similarly, the holes quickly relax to the $V_{\chi=+1}$ band maximum. The radiative recombination of $C_{\chi=-1} \rightarrow V_{\chi=+1}$ is spin-forbidden. Moreover, the $C_{\chi=-1}$ band minimum and the $V_{\chi=+1}$ band maximum are located in different points in the Brillouin zone, creating an indirect bandgap that further slows down the recombination. b. Schematic showing Pb and I displacement in pseudocubic MAPbI$_3$. Pb is grey. I is indigo. Broken circles are original high-symmetry positions. Organic molecules are not shown. c. Phase diagram of splitting energy and spin texture for structures with different Pb and apical I displacements in pseudocubic MAPbI$_3$. The color is the minimum value between the averaged splitting energy of two Rashba conduction bands and two valence bands. The spin texture phase boundaries are indicated by the solid red lines. When the structure transforms from a favorable to an unfavorable spin texture region, the two Rashba valence bands or conduction bands exchange, creating a negative splitting energy. The dashed lines indicate the areas with energy cost less than 25 meV (equivalent to thermal energy at room temperature) to distort Pb and I. The red circle marks the distortions with the lowest total energy. Adapted from Ref. 54.

Concluding remarks.

We have discussed recent advances in the field of \textit{ab initio} modeling of quantum dynamics of photogenerated charge carriers in hybrid perovskites, with special emphasis on the realistic aspects of perovskite atomistic and chemical structure. The considered examples show a great potential of atomistic time-domain simulations for predicting properties and explaining
mechanisms governing efficiencies of active materials for photovoltaics. The simulations generate unique opportunities to separate the effects of various physical, chemical and structural factors. Such knowledge is essential for understanding of complex photo-physical properties of the hybrid perovskite systems. The reported dynamics studies formulate detailed conclusions which may further guide technological efforts towards design of optimal perovskite materials for photovoltaic purposes.

The photoinduced charge carrier cooling timescales for a popular hybrid perovskite, MAPbI$_3$, have been reported by Madjet et al. The calculations reproduced the experimental timescales and identified the phonon modes responsible for the relaxation. The predicted slowdown of carrier dynamics upon chlorine doping and the established mechanism of this effect facilitate the efforts for hot charge carrier extraction.

Long et al. analyzed realistic structural aspects governing performance of perovskite solar cells, including grain boundaries, dopants, surfaces and interfaces with charge acceptors and water. It was found that strong interactions between perovskite and TiO$_2$ facilitate ultrafast photoinduced charge transfer, that Cl and Br doping reduces losses of the photogenerated charges, that grain boundaries provide a major pathway for the charge recombination, and that perovskite interaction with water depends strongly on the amount of water on the perovskite surface. The predicted changes in the charge and energy transfer and relaxation processes arise due to a complex interplay of charge localization, trapping, elastic and inelastic electron-phonon interactions, and thermal disorder.

Jankowska and Prezhdo studied the effect of electric order among the organic cations on electron-hole recombination. The ferroelectric phase demonstrated slower recombination than the paraelectric phase, rationalizing the experimentally observed improved performance of ferroelectric perovskites. The effect was explained by slow, collective oscillations of the polar organic groups in the ferro form.

Zheng et al. demonstrated an interesting possibility for enhancement of charge-carrier lifetimes due to the relativistic Rashba effect. The spin-orbit interaction and out-of-plane displacements of the heavy Pb atoms were found to induce internal electric fields that lifted spin degeneracy of the band-edge states and could lead to an indirect bandgap. The arising necessity of a spin-flip and momentum transfer inhibit charge recombination.
The great progress in the light-to-current conversion efficiency encourages commercialization of hybrid organic-inorganic perovskite solar cells. At the same time, one should be well aware of the major stability concerns of perovskite cells subjected to humidity, electric field and irradiation by light, having strong negative effects on the solar cell performance. The degradation due to exposure to moisture can be partially avoided via device engineering and advanced fabrication techniques by covering the perovskite with other materials, such as graphene, or replacing the organic cation with the Cs atom on the material surface. Interaction between perovskite and electric field, leading to material polarization, and in particular ion diffusion, as well as the photo-degradation problem, require resolution for real device applications, because they undermine the solar cells performance in the long run. The two-dimensional perovskites incorporated in the Ruddlesden-Popper solar cell have shown great stability against humidity and photo-irradiation. The issue of stability under polarization remains largely unsolved and needs further investigation.

The time-domain atomistic simulations of charge carrier dynamics, mimicking directly numerous time-resolved pump-probe experiments provide unique insights into the atomistic mechanisms of the far-from-equilibrium processes taking place in hybrid organic-inorganic perovskites and other solar cells materials. The number of theoretical papers is orders of magnitude smaller than the number of the corresponding experimental publications. In addition to the optical laser experiments probing the dynamics of valence electrons and vibrational modes at the visible, ultra-violet and infrared frequencies that are most relevant for solar energy harvesting, other approaches, such as the terahertz spectroscopy, and the emerging techniques, including time-resolved X-ray and attosecond spectroscopies, can provide additional insights into the coupled evolutions of electrons and nuclei. For instance, terahertz measurements characterize changes in electrical conductivity upon photo-excitation. Time-resolved X-ray can probe directly structural re-arrangements, such as ion diffusion that occurs in perovskites subject to electric fields. Attosecond time-resolution is required to study short-lived quantum coherences that are formed during the initial photo-excitation and the subsequent quantum transitions.

The discussed theoretical studies of quantum dynamics focus largely on the non-radiative, phonon-induced electron-hole recombination, and provide only a glimpse of the capabilities of time-domain atomistic simulations. Future work should incorporate a broader range of perovskites, more complex systems including interfaces of perovskites with various
charge extracting materials\textsuperscript{70,71}, coupling of charge dynamics with ionic transport, longer time-scales, larger systems and other phenomena, e.g. Auger-type charge scattering\textsuperscript{72,73}. It is important to sample appropriately structural changes associated with long time events induced by polaron formation, ion diffusion, surface degradation and electric phase transitions, in order to investigate how such changes influence charge-phonon dynamics. Non-adiabatic molecular dynamics simulations of three and two-dimensional inorganic and hybrid perovskites can characterize in detail the highly non-equilibrium evolutions initiated in the perovskite materials by light absorption and involving various degrees of freedom. Such studies generate valuable knowledge that can form the fundamental basis for improving the performance of perovskite solar cells and related systems.

Biographies

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**Theoretical Models**

NAMD simulations have been carried out with use of the mixed quantum-classical approaches: fewest switches surface hopping (FSSH)\textsuperscript{74} in the case of carrier relaxation\textsuperscript{20}; decoherence-corrected FSSH\textsuperscript{75} for effects of grain boundaries\textsuperscript{38} and chemical doping\textsuperscript{29} on electron-hole recombination studies; and decoherence induced surface hopping (DISH)\textsuperscript{76} for influence on humidity\textsuperscript{44} and local electric order\textsuperscript{49} on charge recombination. In all cases, the classical path approximation (CPA) was used\textsuperscript{77}. The FSSH and DISH calculations have been performed with the PYthon eXtension for the Ab Initio Dynamics software (PYXAID)\textsuperscript{77,78}. The decoherence-corrected FSSH calculations have been done using the original codes\textsuperscript{75,79}. The Rashba-effect on the inelastic phonon scattering rate for electrons and holes has been investigated using Fermi’s golden rule approach\textsuperscript{54}. The geometric and electronic structure of the analyzed systems have been calculated using \textit{ab initio} density functional theory with the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{80,81} exchange-correlation functional, including the Grimme DFT-D2 correction\textsuperscript{82} for the van der Waals interactions.

Although it is acknowledged that hybrid functionals, such as HSE06\textsuperscript{83} increase the accuracy of the non-covalent interactions description, they also significantly increase the computational cost and are generally not affordable for NAMD simulations of the larger HOIPs systems. The chosen PBE functional is widely accepted as one of the best parameter-free density functionals satisfying the key physical and mathematical requirements of DFT. In particular, PBE obeys the Lieb-Oxford bound\textsuperscript{84} and leads to smooth pseudopotentials.\textsuperscript{80,81} Combined with the correction for the van der Waals interactions implemented within the Grimme DFT-D2 method, the PBE functional gives reasonable description of intra- and inter-material interactions within the studied systems.

With the exception of the Rashba-effect study, the spin-orbit coupling (SOC) effects have not been included explicitly during the electronic structure calculations. The scalar-relativistic correction is included in the used pseudopotentials. SOC is recognized to cause a down-shift of
the lowest conduction-band state energies in HOIPs.\textsuperscript{85–87} The resulting reduction in the HOIP bandgap is captured fortuitously by the self-interaction error present in PBE and other pure DFT functionals. Please refer to the cited original papers for further methodological details.

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