ABSTRACT: In this work, we study the role of spin–orbit coupling (SOC) in nonradiative relaxation of hot electrons and holes in methylammonium lead perovskite, MAPbI₃. For this purpose, we have developed the nonadiabatic molecular dynamics method with two-component spinor wave functions that are solutions of the relativistic Kohn–Sham (KS) equations. We find that SOC enhances contributions of Pb(pₓ) and Pb(pᵧ) orbitals to the conduction and valence bands. As a result, the KS orbitals become more sensitive to nuclear motions, leading to the increased nonadiabatic couplings. Consequently, SOC greatly speeds up the electron and hole relaxation, making the computed relaxation time scales consistent with available experiments. We suggest that the fast hot carrier relaxation facilitated by the SOC allows rapid transition into the long-lived triplet state that extends charge-carrier lifetime and helps achieve high-efficiency perovskite solar cells.

Photovoltaic (PV) materials enable efficient conversion of solar energy to electricity, offering to reduce the world’s consumption of fossil fuels and make clean and sustainable energy production an everyday reality. Considerable efforts have been devoted to developing new generations of solar cells. In particular, perovskite materials have gained a lot of attention from the scientific community lately. Among them, methylammonium lead halide perovskites, MAPbX₃ (X = Cl, Br, I), have been under increasing studies in the past few years. Perovskite materials have a tunable band gap, long carrier diffusion length, and high carrier mobilities and are inexpensive to manufacture. Many investigations of perovskite materials were carried out from experimental and theoretical viewpoints. Most theoretical works studied properties including the role of defects, mechanisms of ionic migration, dynamic disorder, optical and electronic structure properties, or the original and doped systems.

A number of theoretical investigations of nonadiabatic molecular dynamics (NA-MD) have been undertaken using nonrelativistic density functional theory (DFT) calculations. At the same time, relativistic effects are expected to play an important role in such systems, because they contain heavy elements such as lead or iodine. The giant spin–orbit coupling (SOC) that notably influences the band structure of perovskite materials has been reported in previous work. This effect leads to the band gap reduction in such systems by as much as 1 eV, generating nondegenerate spin states, long-lived triplet states, and a room-temperature Rashba splitting effect. However, the effects of SO interactions on charge-transfer (CT) and energy-transfer (ET) dynamics remain largely unexplored to date. An understanding of these effects could provide further insights into the prominent performance of perovskite-based solar cells.

In this work, we aim to fill the indicated void in our knowledge of nonadiabatic dynamics in the presence of SO interactions. In particular, we focus on the role of SOC in hot carrier relaxation dynamics in tetragonal phase MAPbI₃ (Figure 1). To assess the role of the SOC, we have extended the earlier NA-MD procedure to two-component spinor orbitals that are solutions of the relativistic Kohn–Sham (KS) equations. We compare the relaxation rates for electrons and holes.
The NACs are represented by Slater determinants and valence band (VB) orbitals. The increase of the p-type hopping, as computed with the Quantum Espresso (QE)45 method with the KS orbitals computed with and without SOC. Our results indicate that, consistent with previous reports, SOC reduces the band gap by ∼1 eV by affecting the Pb-p contribution in the conduction band (CB) and valence band (VB) orbitals. The increase of the p$_x$ and p$_y$ projections relative to p$_z$ of Pb leads to variation of the nonadiabatic coupling (NAC). As a result, the SOC enhances the electron and hole relaxation rates within the CB and VB, respectively ("cooling"), because of the enlarged NACs and stronger coupling to low-frequency phonon modes. The time scales computed when the SOC effects are accounted for are observed to be in a better agreement with the experimentally derived time scales.2 The accelerated dynamics in the mixed-spin states (relativistic wave functions) suggests a fast population of the superposition states that have a non-negligible triplet states contribution by decay of the initially prepared hot electrons. We hypothesize that the subsequent decoherence of generated superposition of singlet and triplet configurations results in a formation of a notable fraction of triplet electrons, whose recombination with the holes of singlet spin symmetry is notably inhibited. We suggest this mechanism as a possible rationalization of the remarkable solar energy conversion efficiency of lead halide perovskites. Our work indicates that SOC effects cannot be neglected if accurate modeling of the hot carrier relaxation in MAPbI$_3$-based materials is to be performed.

The essentials of the FSSH algorithm and its implementation within the neglect of back-reaction (NBRA) approximation have been presented in detail elsewhere.43,44 Here, we reiterate the key constructs for completeness and then focus only on the elements of the methodology that change in the spin–orbital case. First, the overall time-dependent wave function of the system is represented as a spin-adiabatic basis:

$$\Psi = \sum_i c_i(t) \Phi_i(R(t))$$

(1)

Here, the spin-adiabatic basis states, $\Phi_i(R(t))$, are represented by Slater determinants composed of spin–orbitals, $\psi_i$, of N electrons, parametrically dependent on nuclear trajectories, R(t). The spin–orbitals, $\psi_i$, are the eigenvalues of the KS equations with the Hamiltonian that includes the SOC terms, as computed with the Quantum Espresso (QE)45 electronic structure code:

$$(\hat{H}^{KS} + \hat{H}^{SOC})\psi_i^{ad} = \epsilon_i^{ad} \psi_i^{ad}$$

(2)

Within the noncollinear magnetism framework, the orbitals, $\psi_i$, are represented in the form of two-component spinors, which naturally mix $\alpha$, $\phi_i^\alpha$, and $\beta$, $\phi_i^\beta$, components

$$\psi_i = \phi_i^\alpha \alpha + \phi_i^\beta \beta = \left[ \phi_i^\alpha \phi_i^\beta \right], \quad i = 1, ..., N$$

(3)

The evolution of the time-dependent amplitudes, $c_i(t)$, of the above-defined basis states is determined by solving the time-dependent Schrödinger equation (TD-SE):

$$i\hbar \frac{\partial c_i}{\partial t} = H_{el} c_i$$

(4)

Here $H_{el}$ is the vibronic Hamiltonian matrix: $H_{el} = H_{el} - i\hbar d_{el}$. The vibronic Hamiltonian is composed of the electronic Hamiltonian, $H_{el}^{fi} = \langle \Phi | H_{el}^{fi} | \Phi \rangle$, and scalar (time-derivative) nonadiabatic couplings (NACs), $d_{el} = \langle \Phi | \frac{\partial}{\partial t} | \Phi \rangle$. The NACs are computed using the finite difference Hammes-Schiffer and Tully (HST) scheme:47

$$d_{el}(t + dt) = \frac{\langle \Phi(t)|\Phi(t + dt)\rangle - \langle \Phi(t + dt)|\Phi(t)\rangle}{2dt}$$

(5)

As has been suggested earlier43,44, this formula can be reduced to the analogous expression involving only the one-electron KS spin–orbitals. The procedure to compute the overlaps of the crystal orbitals expressed in terms of the plane waves has been elaborated earlier. The distinctive element of the present approach is that such computations must be performed with the two-component spinors. Such calculations can be regarded as computing the dot product of the $2 \times 1$ Hilbert space vectors:

$$\langle \psi(t)|\psi(t') \rangle = \langle \phi_i^\alpha(t)|\phi_i^\beta(t') \rangle \phi_i^\alpha(t') \phi_i^\beta(t')$$

(6)

The geometry optimization and electronic structure calculations have been carried out with the VASP code.48,49 The lattice constant of the tetragonal MAPbI$_3$ simulation cell was kept fixed at its experimental value of $a = b = 8.8$ Å and $c = 12.68$ Å50 during the geometry optimization. After the optimization of the geometry at 0 K, the system is thermalized to 300 K for a 2 ps NVE-MD with a scheduled velocity rescaling to achieve the desired temperature. This is followed by a 3 ps NVE-MD to obtain the nuclear trajectories. A nuclear integration time step of 1 fs is utilized. Calculations of projected densities of states (pDOS) and NACs are carried out at the ab initio level, using the Quantum Espresso (QE) program.46 The SOC effect is introduced by performing the noncollinear calculation using fully relativistic pseudopotentials. Bare DFT functional, PBE, and plane wave basis are used for all calculations. SOC effects are not included in VASP calculations because it does not affect the structural parameters.51,52 The generated MD trajectories are utilized to compute NACs for all pairs of orbitals spanning a several electronvolt energy window around the fundamental band gap.
The present work employs the SOC-enabled NA-MD implemented in the PYXAID2 program.53 The implementation relies on the modular library for nonadiabatic and quantum dynamics simulations, Libra.54 The latter implements the routines for surface hopping, statistics analysis, and functions for reading and parsing the output of Quantum Espresso calculations. Further details of the employed methodologies and algorithms can be found in the Supporting Information.

Using the optimized (zero-temperature) geometry, we compute the projected densities of states (pDOS) with and without SOC included (Figure 2). We specifically resolve the s- and p-contributions of Pb and I atoms. Pb-d orbital is not presented because it is an extremely deep position.55 The band gap of \(\sim 1.59\) eV is obtained at the \(\Gamma\)-point when SOC is excluded. The inclusion of SOC decreases the gap by \(\sim 1\) eV, down to approximately 0.56 eV, in agreement with previous investigations performed at a similar level of theory.42 The band gap reduction is mainly achieved by shifting the CB edge. It has been well-established that the bare DFT provides a fortuitous band gap compared with experimental value because of error cancellation between bare DFT and neglect of the SOC effect.52 De Angelis et al. have reported the value of 1.67 eV obtained at a more advanced level of the theory, using the GW/SOC approach.52 The GW correction is not required in our simulation because we are not modeling the transition across the band gap, and such implementations are time-demanding for NAC computations which require thousands of electronic structure calculations.

The computed pDOS shows an asymmetric distribution, such that the VBs are denser than the CBs. Small DOS favors slower carrier relaxation.56 The pDOS shows that the VBM consists of antibonding hybrids of Pb-6s and I-5p states, whereas the CBM is composed mostly of the Pb-6p state. SOC notably increases the contributions of \(p_x\) and \(p_y\) states of the Pb atom to the VB and CB states (see Figure S1). This is further evidenced by the analysis of charge density plots for a number of selected KS orbitals (Figure 2, right panels); without SOC, the \(p_z\) orbital of Pb atoms hybridize with \(p_x\) and \(p_y\) orbitals to a smaller extent. The orbital hybridization is substantially enhanced by SOC. The mechanism of hybridization enhancement involves the inversion symmetry-breaking (ISB) field along the \(z\) direction induced by SOC allowing the hopping between the \(p_z\) (or \(p_x\)) with \(p_x\) orbitals, causing the significant mixing of the three states.57

The modulation of electronic structure by SOC is expected to affect the NACs, because the latter scale inversely with the

![Figure 2. Projected density of states (pDOS) and charge density for selected KS orbitals involved in electron and hole relaxation without (top) and with (bottom) SOC based on the optimized ground-state structure. The calculations are performed with QE code using a \(9 \times 9 \times 9\) k-points grid. Zero energy of the energy scale is set to the Fermi energy of the system. VBM-11 locates at \(\sim 1\) eV below the VBM. SOC enhances the coupling of in-plane \(p_x\) and \(p_y\) orbitals with out-of-plane \(p_z\) orbital of Pb atoms, leading to significant overlap of the three components, see Figure S1.](image1.png)

![Figure 3. Visualization of the averaged nonadiabatic couplings (NACs) between states in orbital indices for without (a) and with (b) SOC cases (meV). SOC significantly affects the NAC magnitude of CB and higher VB states because they have considerable contributions from Pb-6p states.](image2.png)
corresponding energy gaps. To assess this effect, we have computed the average magnitudes of NACs of the two types. In doing this, we have utilized the identical nuclear trajectories as well as the identical electronic structure simulation protocols, other than the inclusion of SOC. A comparison of the 2D maps, showing NACs between all pairs of states within the spaces of KS orbitals considered in our calculations, is presented in Figure 3. The averaged NACs are computed as

\[ \langle \text{Im}(H_{\alpha \beta,ij}) \rangle = \langle \hbar/T \rangle \sum_{t=0}^{T-1} |d_{ij}(t)| \]  

Here, \( T = 3000 \) is the number of MD steps, \( H_{\alpha \beta,ij} \) a matrix element of the vibronic Hamiltonian defined after eq 4, \( d_{ij}(t) \) an instantaneous NAC matrix element, and \( \hbar \) Planck's constant (\( \hbar = 1 \) in atomic units used here); \( \langle \rangle \) denotes the time averaging. The rate of electronic transition depends on the NAC elements \( d_{ij} \). A larger \( d_{ij} \) corresponds to faster electronic transition between state \( i \) and \( j \). In both types of calculations, the largest NACs are positioned at the first subdiagonal, suggesting that the energetically close states are the ones that couple to each other most strongly. The couplings gradually decrease, as the states are energetically separated, indicating that the dominant nonradiative relaxation process involves the consecutive population-transfer mechanisms. The numerical data are summarized in Table S1.

The inclusion of SOC has two main effects. First, it increases the average magnitudes of NACs. This can be explained by the nature of the two-component functions: because they represent superpositions of electrons/holes in \( \alpha \) and \( \beta \) states, it is reasonable to expect that these orbitals have lesser repulsion than the spatial components of same-spin orbitals. Such an “extended” size of the resulting SOC-based orbitals is clear from Figure 2. Because of the increased spatial overlap of different orbitals, the time-overlaps, eq 6, and the NACs, eq 5, increase. The second effect concerns the qualitative changes of the NAC structure. As Figure 3b shows, there is a substantial degree of coupling of states within either CB or VB. Unlike in the case without SOC enabled, the states do not have to be energetically close to experience notable NAC between them. This effect can be explained by the “mixing” of the spin-diabatic orbitals by the \( H_{\text{SO}} \) operator. In the context of perturbation theory, the \( H_{\text{SO}} \) Hamiltonian couples several spin-diabatic (eigenfunctions of spin-free Hamiltonian) states in a single spin-adiabatic superposition, \( \psi_{i \text{adi}} = \sum_j c_{ij} \psi_{j \text{dia}} \). The NACs in the spin-adiabatic basis, \( d_{ij} \text{adi} = \langle \partial_t \psi_i \text{adi} | \partial_t \psi_j \text{adi} \rangle \), are then expressed as linear combinations of the corresponding NACs between spin-diabatic states, \( d_{ij} \text{dia} = \langle \psi_i \text{dia} | \partial_t \psi_j \text{dia} \rangle \). As Figure 3a suggests, the latter are coupled locally; each state is coupled only with a few energetically close states. However, because \( d_{ij} \text{adi} \) is a linear combination of multiple \( d_{ij} \text{dia} \), more energetically distant states become notably coupled.

The energy decay of the “hot” electrons and holes computed with and without consideration of SOC interactions in NAMD are presented in Figure 4. In general, electron and hole energy relaxes much faster with SOC than without it. Particularly, when SOC is not included, we do not observe the apparent decay of electron energies within the 2.5 ps time scale of our simulation. The relaxation of highly energetic holes occurs on the order of 2 ps and is only weakly dependent on their initial energy. The accelerated relaxation of holes in

![Figure 4](image-url)
contrast to that of electrons may be attributed to their higher densities of states, as is suggested by the pDOS (Figure 2). Once the SOC is included, both electrons and holes undergo fast relaxation, on a $200\text{−}300$ fs time scale, in agreement with photoluminescence experiments which suggest $\sim 400$ fs hole relaxation time scales. Interestingly, the inclusion of SOC accelerates the relaxation of both holes and electrons, making both processes less sensitive to densities of states. The observed acceleration is a direct consequence of the increased NACs in the treatment that incorporates SO interactions. It is worth mentioning that nonradiative electron−hole recombination across the band gap takes place on the hundreds of nanoseconds time scale and is not considered in this work.

The phonon modes are computed via Fourier transform (FT) of the autocorrelation functions of fluctuation of energy difference between pairs of states, according to the optical response function formalism of Mukamel. The computed influence spectra illustrate the phonon modes that drive particular pairs of transitions. As Figure 5 suggests, the inclusion of SOC can notably change the spectra. Note that because the two types of spectra (with and without SOC) are obtained from identical nuclear trajectories, the difference in the influence spectra originates from the change of the electronic structure, not because of possible changes of nuclear dynamics. In particular, the inclusion of the SOC Hamiltonian causes the one-electron orbitals (spin-adiabatic) to be linear combinations of spin-diabatic orbitals, which are eigenfunctions of a spin-free Hamiltonian. This mixing of the spin-diabatic states translates not only into NACs, as discussed above, but also into the influence spectra (Figure 5). In earlier work reporting simulation of electron−hole recombination in MAPbI$_3$, the low frequency below $100$ cm$^{-1}$ arising from Pb−I stretching and I−Pb−I bending was found to dominate the FT spectrum: charge recombination couples little to the vibration of the organic cation. In the present work, we observe a similar relationship both for electron and hole intraband relaxation. In general, the electronic transition between adjacent states couple more strongly to the vibration of the inorganic cage for electron and hole relaxation with SOC, an indication of the larger NAC. Overall, the low-frequency modes dominate the FT spectrum for electron and hole relaxation processes.

So far, we have demonstrated that Pb and I-induced SOC in MAPbI$_3$ accelerates a transition between different two-component spinors of the system. It is interesting to know how this helps generate long-lived charge carriers, which are important for improved power conversion efficiencies in perovskite solar cells (Figure 6). First, the photon absorption generates an excitation by primarily promoting an electron of one spin symmetry (not changing the spin character of the system). The photoexcited electron can now either recombine with the hole (spin-allowed) or can evolve in the manifold of the spin-adiabatic (mixed spin states) leading to a new wave function with distinct overall spin symmetry ("coherent evolution"). This wave function can be represented by a coherent superposition of singlet and triplet configurations. This process contains both adiabatic and nonadiabatic components, but it is possible only in the presence of SO interactions.
coupling (SOC-enabled). The evolved superposition can decohere, which can be regarded as generation of a mixture of different spin-symmetry excitations (singlet and triplet electron/hole pairs). The singlet electron/hole (e/h) pair can experience a fast recombination, because it is spin-allowed. At the same time, the triplet e/h pair remains long-lived because its recombination is spin-forbidden.

As it follows from the proposed mechanism, the fast coherent evolution of the spin-adiabatic states enables the SO interactions is important in two aspects. First, it reduces the chances of electron−hole recombination, because it opens another “reaction” channel. Second, SOC enables evolution of mixed-spin states, which eventually enables generation of triplet configurations. As a result, these factors may improve the photocurrent density generated in perovskite-based materials. Indeed, recent experiment showed that the replacement of Pb with Sn in perovskite could reduce SOC, decreasing the single-to-triplet conversion efficiency and lowering the photocurrent density. Thus, we conclude that the fast coherent evolution of the mixed-spin state charge carriers is essential for improved performance of PV materials via enabling generation of the long-lived triplet states.

In summary, we have investigated the effect of SOC on the electron and hole relaxation in perovskite MAPbI_3. Our results show that SOC enhances the contribution of the p_x and p_y orbitals of Pb atoms to the CB and VB states, leading to the larger NAC. SOC greatly speeds up the electron and hole relaxation, particularly, producing time scales in agreement with the available experimental data. Hole relaxation is faster than electron relaxation because VB states are denser than CB states. The difference in the relaxation rate can be explained by the increased NAC, which grows because the KS orbitals show stronger dependence on nuclear coordinates as a result of the enhanced contributions of the p_x and p_y orbitals of Pb. SOC does not change the nature of the phonon modes that couple to the charge carriers. Both electrons and holes couple primarily to low-frequency phonon modes, involving vibrations of Pb and I atoms. Finally, we propose a mechanism by which the SOC-accelerated NA dynamics in the manifold of spin-adiabatic states may favor generation of longer-lived charge carrier pairs to improve the PV characteristics of such materials.

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