Nonlocal Screening Dictates the Radiative Lifetimes of Excitations in Lead Halide Perovskites

Yoonjae Park, Amael Obliger, and David T. Limmer*

Cite This: https://doi.org/10.1021/acs.nanolett.2c00077

ABSTRACT: We use path integral molecular dynamics simulations and theory to elucidate the interactions between charge carriers, as mediated by a lead halide perovskite lattice. We find that the charge—lattice coupling of MAPbI$_3$ results in a repulsive interaction between electrons and holes at intermediate distances. The effective interaction is understood using a Gaussian field theory, whereby the underlying soft, polar lattice contributes a nonlocal screening between quasiparticles. Path integral calculations of this nonlocal screening model are used to rationalize the small exciton binding energy and low radiative recombination rate observed experimentally and are compared to traditional Wannier—Mott and Fröhlich models, which fail to do so. These results clarify the origin of the high power conversion efficiencies in lead halide perovskites. Emergent repulsive electron—hole interactions provide a design principle for optimizing soft, polar semiconductors.

KEYWORDS: Lead halide perovskite, excitons, charge carrier lifetime, path integral molecular dynamics, Gaussian field theory

L
ead halide perovskites are a class of materials that have unique photophysical properties resulting from their soft, polar lattices. They have vanishingly small exciton binding energies and despite modest mobilities, have large free carrier diffusion lengths resulting from exceptionally long carrier lifetimes.\(^1\)\(^-\)\(^3\) These properties make lead halide perovskites ideal materials for photovoltaic devices.\(^4\)\(^-\)\(^6\) Many of their optoelectronic properties have been thought to arise from electron—phonon coupling, as the largely ionic bonding of the lead halides admit strong Coulomb interactions between free charges and the lattice. It has been conjectured that polaronic effects in particular,\(^7\)\(^-\)\(^10\) act to protect free charges from recombination and screen their interactions, reducing exciton binding energies.\(^11\) However, the significant anharmonicity of the perovskite lattice has made uncovering the molecular origin of these properties difficult.\(^11\)\(^-\)\(^14\)

Here, we apply path integral molecular dynamics,\(^15\)\(^,\)\(^16\) to study an atomistic model of quasiparticles embedded in a MAPbI$_3$ lattice, in order to understand how a fluctuating lattice affects its electronic properties. Much recent effort has gone into understanding the effects of the lattice on the excitonic properties of perovskites computationally,\(^17\)\(^-\)\(^20\) and analytically.\(^16\)\(^,\)\(^21\) However, unlike traditional polar semiconductors where lattice fluctuations can be described by a harmonic approximation, the tilting and rocking motions of the inorganic octahedra\(^14\) and nearly free motions of the A-site cations\(^12\)\(^,\)\(^13\) render the lattice highly anharmonic. This complicates the simplification to traditional model Hamiltonians like the Fröhlich model or its generalizations.\(^20\)\(^,\)\(^22\) Attempts to include lattice effects into \textit{ab initio} based approaches have been developed, but these are difficult to extend to the time and length scales necessary to explain the nature of how photogenerated electrons and holes bind, dissociate, and recombine.\(^23\) Using an explicit atomistic representation of the lattice surrounding the quasiparticles allows us to go beyond simplified models. Employing path integral calculations allows us to consider finite temperature effects directly on diffusive time and length scales. These simulations motivate a field theory to describe the effective electron—hole interactions that dictate the emergent optical properties of the perovskites. With these simulations and theory, we are able to elucidate the origin of low exciton binding energies and recombination rates as a consequence of a nonlocal screening from the lattice.

We consider a system of an electron—hole pair, interacting with a MAPbI$_3$ perovskite in its cubic phase employing a fully atomistic description of the lattice. The full system Hamiltonian, $\mathcal{H}$, consists of electronic, lattice, and interaction pieces, $\mathcal{H} = \mathcal{H}_{\text{el}} + \mathcal{H}_{\text{lat}} + \mathcal{H}_{\text{int}}$. The highly dispersive bands of MAPbI$_3$ allow us to make an effective mass approximation, so that the electronic Hamiltonian is defined as

Received: January 10, 2022
Revised: February 25, 2022
where the subscripts e and h indicate electron and hole, \( \hat{p}_e \) and \( \hat{r}_e \) are the momentum and position operators, \( m_e/m = m_h/m = 0.2 \) are the band masses of the quasiparticles taken from recent GW calculations in units of the bare electron mass \( m_e^0 \). \( \varepsilon_0 \) is the vacuum permittivity, and \( \varepsilon_\infty \) is the optical dielectric constant for charge e. For the lattice, we use an atomistic model developed by Mattoni et al. that has been demonstrated to reproduce the structural and dielectric properties of lead halide perovskites.\(^{23,26}\) Its Hamiltonian is decomposable as

\[
\mathcal{H}_l = \sum_{i=1}^{N} \left( \frac{\hat{p}_i^2}{2m_i} + \frac{U_i(\hat{r}_i^N)}{2} \right) + \sum_{i<j} U_{ij}(\hat{r}_{ij})
\]

where \( \hat{p}_i \) and \( m_i \) are the momentum, position, and mass of ith atom, \( N \) is the total number of atoms in the lattice, and \( U_i(\hat{r}_i^N) \) is the pairwise interaction potential between atoms with configuration \( \hat{r}_i^N = (\hat{r}_{i1}, \hat{r}_{i2}, ..., \hat{r}_{in}) \). The potential includes electrostatic and excluded volume interactions. The charge–lattice interaction term is given by \( \mathcal{H}_{\text{latt}} = \sum_{i} U_{ei}(\hat{r}_e, \hat{r}_i) + U_{hi}(\hat{r}_h, \hat{r}_i) \) where \( U_{ei} \) and \( U_{hi} \) denote sums of pseudopotentials. Consistent with the largely ionic nature of MAPbI\(_3\), we employ pseudopotentials of the form of short-ranged truncated Coulomb potentials, with a cutoff radii chosen as the ionic radii of each species.\(^{27-29}\)

As the atoms are heavy and we are largely interested in room temperature behavior, we adopt a classical description of the MAPbI\(_3\) lattice. We discuss below corrections to this classical approximation in the harmonic lattice limit. For the two light quasiparticles, however, we employ a path integral description to account for quantum mechanical effects important even at room temperature. Such a quasiparticle path integral approach has been employed previously to study lattice effects in the lead halides and trapping in other semiconductors.\(^{30-33}\) The partition function, \( \mathcal{Z} \), for the composite system can be written as

\[
\mathcal{Z} = \int \mathcal{D}[\hat{r}_e, \hat{r}_h, \hat{r}_i^N] e^{-S[i(\hat{r}_e, \hat{r}_h, \hat{r}_i^N)]}/\hbar
\]

with the action \( S[\hat{r}_e, \hat{r}_h, \hat{r}_i^N] = S_{\text{el}} + S_1 + S_{\text{int}} \). The corresponding imaginary time path action for the electronic part becomes

\[
S_{\text{el}} = \int_0^T m_e \frac{\hat{r}_e^2}{2} + m_h \frac{\hat{r}_h^2}{2} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_\infty (\hat{r}_e^2 - \delta_{\hat{r}_e})} \tag{4}
\]

where the imaginary time \( \tau \) is defined over the interval 0 to \( \beta \hbar \), \( \beta^{-1} = k_\text{B}T \), \( T \) is temperature, \( k_\text{B} \) is Boltzmann’s constant, and \( \hbar \) is Planck’s constant. The velocity and position of electron/hole are denoted \( \hat{v}_e/h_e \) and \( \hat{r}_e/h_e \). Under the assumption of a classical lattice, the contributions to the path action from MAPbI\(_3\) and its interaction with the quasiparticles become \( S_1 = \beta \hbar \mathcal{H}_l \) and

\[
S_{\text{int}} = \int_0^T U_{ei} (\hat{r}_e, \hat{r}_i) + U_{hi} (\hat{r}_h, \hat{r}_i) \tag{5}
\]

an integral over the pseudopotentials. When the path action is discretized into a finite number of imaginary time slices, the classical counterpart of each quantum particle becomes a ring polymer consisting of beads connected by harmonic springs.\(^{35}\)

We perform molecular dynamics (MD) simulations of two ring polymers with 1000 beads representing the electron and hole and a MAPbI\(_3\) lattice with 40 × 15 × 15 unit cells at 300 K. The large system size is necessary in order to ensure that self-interaction errors between the quasiparticles are minimized. This atomistic description allows us to capture all orders of interaction between the quasiparticles and the MAPbI\(_3\) lattice, free of low temperature harmonic approximations. The simulation details including pseudopotentials and the force field of the lattice can be found in Supporting Information (SI section 1).

To analyze the emergent exciton interaction resulting from the collective motions in MAPbI\(_3\), we compute the free energy between electron and hole using Umbrella sampling with the Weighted Histogram Analysis Method.\(^{33}\) We compute the reversible work to move two charge centers relative to each other

\[
\beta F(R) = -\ln(\delta(R - r_e^c - r_h^c)) \tag{6}
\]

where \( R \) is the distance between the electron and hole centroid \( r_e^c, r_h^c \). \( \delta(x) \) is Dirac’s delta function, and \( \langle ... \rangle \) represents an ensemble average. Simulation snapshots are shown in Figure 1a,b, where spatially delocalized charges extend with a radius of gyration between 1.5 and 3 nm. Figure 1c shows \( F(R) \), which is nonmonotonic. The free energy exhibits a minima at \( R = 0 \) reflecting the binding of the electron–hole pair into an exciton, a plateau at large \( R \), and a barrier at intermediate \( R \approx 8 \) nm. The binding energy is large due to the neglect of polarizability in this description of the lattice. Considering the bare

\[ \text{Quasiparticle path integral molecular dynamics simulations.} \]

Representative snapshots of the simulation of electron (red) and hole (blue) with the MAPbI\(_3\) lattice where the electron and hole are (a) close to and (b) far from each other. Zoomed in structure in (a) represents the MAPbI\(_3\) lattice where gray, yellow, and blue atoms represent Pb\(^{2+}\), I\(^{-}\), and MA\(^{+}\), respectively. (c) Free energy between electron and hole as a function of the distance between quasiparticle centroids from molecular dynamics simulation (black circles) and an effective exciton interaction from eq 13 (red solid line) with parameters as \( e^* = 5, l_1 = 2.47 \) nm, and \( l_2 = 1.26 \) nm.
Coulomb potential is a monotonic function, the repulsive interaction found in Figure 1c at intermediate electron—hole distances must arise from the lattice. An effective electron–hole repulsion has been speculated in lead halide perovskites previously\textsuperscript{36–38} but had defied direct observation or theoretical validation.

In order to understand the emergent lattice effects on the electron—hole interaction and surprising intermediate repulsion, we assume that the fluctuations of the lattice are well described by a Gaussian field. Such Gaussian field theories underpin a number of standard effective interactions including dielectric continuum theory and the Casimir effect.\textsuperscript{39–41} A Gaussian approximation in this context is analogous to the quasi-harmonic approach\textsuperscript{42} where it is assumed that while the lattice is anharmonic, it responds linearly.\textsuperscript{43,44} We consider approximating the lattice by an effective polar displacement field, $u_{k}e_{r}$, which is expected to be correlated with local bending and rocking motions of the octahedra.\textsuperscript{45} Within the Gaussian field approximation, the path action for the lattice becomes

$$S_{l} \approx \frac{1}{2} \int \int \int \int \int \frac{u_{k} \cdot \Delta \chi^{-1} \cdot u_{k} \cdot r}{k}$$

(7)

where $\chi^{-1} \cdot r$ is the susceptibility at wave vector $k$ and imaginary time displacement $\tau \rightarrow \tau'$. The susceptibility is determined by a phonon dispersion relationship only in the limit of zero temperature, and generally reflects the correlations within the effective polar displacement field.\textsuperscript{46} Consistent with the Coulombic pseudopotentials used in the MD simulations, we take the coupling between the charges and the lattice to be linear

$$S_{\text{int}} \approx \int \int \int \int \int \frac{u_{k} \cdot \Delta \chi^{-1} \cdot u_{k} \cdot r}{k}$$

(8)

and described by a Fröhlich-like interaction,\textsuperscript{47} where $\lambda$ is a Fröhlich coupling constant. The lattice variables can be integrated out, leaving a Gaussian approximation to the partition function, $Z_{G}$,

$$Z_{G} = \int \mathcal{D}[\mathbf{r}, \mathbf{u}_{0}] e^{-S_{\text{int}}[\mathbf{r}, \mathbf{u}_{0}] / \hbar}$$

$$= Z_{l} \int \mathcal{D}[\mathbf{r}_{l}] e^{-S_{l} / \hbar} e^{-S_{\text{int}}[\mathbf{r}_{l}] / \hbar}$$

(9)

where $Z_{l}$ is the partition function for a displacement field without couplings to the charges. This integration results in an effective path action of the form (see the SI for details)

$$S_{\text{eff}} = -\sum_{ij} \int \int \mathcal{D}[\mathbf{r}_{ij}] \frac{1}{\delta} \left| \mathbf{r}_{ij} \right|^{2} e^{-\alpha \left| \mathbf{r}_{ij} \right|}$$

(10)

where $i, j \in \{e, h\}$ and $\Gamma_{ij}$ takes the value of $\Gamma_{ij} = 1$ if $i = j$ and $\Gamma_{ij} = -1$ if $i \neq j$.

The susceptibility $\chi_{k}$ is proportional to a dielectric function evaluated in the absence of the quasiparticles. Different functional forms of its imaginary time and wavevector dependence imply different ways in which the lattice can screen the quasiparticles. In the classical limit,\textsuperscript{48} $\chi_{k} = \chi_{k} \delta(\tau)$, eqs 4, 10, and 12, imply an effective interaction between the electron and hole,

$$\hat{V}_{\text{eff}}(k) = -\frac{1}{k^{2}} \left[ \frac{e^{2}}{e_{\infty}} - \chi_{k} \left| \mathbf{r}_{ij} \right|^{2} \right]$$

(11)

which is a sum of the bare interaction, here screened by $e_{\infty} = 4.5$,\textsuperscript{49} and the contribution from the lattice proportional to $\chi_{k}$. In the zero wavevector limit, this is a constant, and if taken as $\chi_{k} \left| \mathbf{r}_{ij} \right|^{2} / e_{\infty} \left( 1 / e_{\infty} - 1 / e_{\infty} \right)$, we recover the Wannier–Mott model of a exciton. With an effective dielectric constant $e_{\infty} = 6.1$,\textsuperscript{24} this local, static screening is manifestly insufficient to produce the repulsive interaction observed from the free energy calculations. Rather an explicit $k$ dependence to $\chi_{k}$ is required.

Using explicit MD simulations of the bulk classical MAPbI\textsubscript{3} lattice, we find $\chi_{k}$ well approximated by

$$\chi_{k} \approx \frac{\chi_{0}}{1 - l_{r}^{2}k^{2} + l_{l}^{2}k^{2}}$$

(12)

characterized by three positive real parameters, $\chi_{0}$, $l_{r}$ and $l_{l}$. This functional form includes a single resonant peak and is assumed isotropic on length scales greater than the lattice spacing. The resonant peak results from the negative second-derivative polar displacement $\delta_{ij}$, where the phonon mode is characterized by a single longitudinal optical frequency $\omega$. Performing the inverse Fourier transform gives an effective potential

$$V_{\text{eff}}(r) = -\frac{e^{2}}{4\pi e_{\infty}} \left[ \frac{1}{e_{\infty}} + \frac{\gamma}{4\delta e_{\infty}} \sin[\gamma r - \theta] \right]$$

(13)

where $r$ is the distance between two charges. Details of the derivation with analytic expressions for $1/e_{\infty}$ and $\gamma$ are shown in the SI section II. This form is plotted in Figure 1c and provides an excellent fit at large $r$ to the free energy from the MD simulation. We refer to this effective electron–hole interaction arising from spatially dependent screening from the MAPbI\textsubscript{3} lattice as nonlocal screening.\textsuperscript{50} The theory clarifies that the nonmonotonic interaction potential results from deformations generated within the lattice due to the charges. At specific characteristic distances these deformations are sufficiently unfavorable that the electron and hole are effectively repelled from each other.

This effective interaction in eq 13 is distinct from what has been considered previously by Pollmann and Buttner,\textsuperscript{51} and by Gerlach and Luczak\textsuperscript{48} in which coupling to a single dispersionless optical phonon results in an excitonic polaron that screens the bare Coulomb potential. In their approximation, the polaron displacement field is treated quantum mechanically by including a $\tau$ dependence of the susceptibility. In Pollmann and Buttner’s work, this is taken as the bare susceptibility,

$$\chi_{k} = \frac{1}{2\alpha} e^{-\alpha \left| \mathbf{r}_{ij} \right|}$$

(14)

where the phonon mode is characterized by a single longitudinal optical frequency $\omega$. Plugging eq 14 into eq 10, we obtain the effective path action

$$S_{\text{eff}} = -\sum_{ij} \int \int \frac{1}{2\alpha} \frac{\omega}{\sqrt{8\pi m_{e}}} \int \int e^{-\alpha \left| \mathbf{r}_{ij} \right|}$$

(15)

where we have written $\left| \mathbf{r}_{ij} \right|^{2}$ in the traditional Fröhlich form, introducing $\alpha$ as the dimensionless coupling constant. Pollmann and Buttner further approximate this dynamic screening approach in order to obtain a closed form effective potential. Their potential is an exponentially screened

https://doi.org/10.1021/acs.nanolett.2c00077

Nano Lett. XXXX, XXX, XXX--XXX
Coulomb potential in the classical limit with a screening length given by the polaron radius. While for certain parameters it is possible that the Pollmann–Butter potential is repulsive, employing known values for \( \alpha = 1.72 \) and \( \omega = 40 \text{ cm}^{-1} \) for MAPbI\(_3\), the resultant effective potential is monotonic and inconsistent with our MD result. Analogous approaches including sums of two or three dispersionless phonons similar fail to describe a repulsive interaction. Treating the susceptibility variationally, Gerlach and Luczak provided a more flexible description of the lattice, but the lack of a wavevector dependence to \( \chi \) still prohibits an intermediate length scale repulsion.

To investigate the implication of a nonlocal screening on the observable properties of MAPbI\(_3\), we simulated an electron and hole pair using our quasiparticle path integral approach under (i) static, (ii) dynamic, and (iii) nonlocal screenings. In each case, we employed known experimental parameters for the dielectric constants, optical frequencies, and effective masses and thus expect our results to be quantitatively accurate. To our knowledge the \( k \)-dependent dielectric susceptibility has not been reported for MAPbI\(_3\), so we parametrized the nonlocal screening interaction using our MD results. For each case, we extract the exciton binding energies and bimolecular recombination rates as both have been difficult to reconcile theoretically.

The exciton binding energy, \( \Delta E_B \), is defined within our path integral framework as

\[
\Delta E_B = \lim_{T \to 0} \min_k \Delta F(R)
\]

and to evaluate it we computed the free energy \( \Delta F(R) = F(R) - F(\infty) \) at a variety of temperatures ranging from 100 to 400 K and extrapolate its value to 0 K (SI Figure S2). Representative free energies at \( T = 300 \text{ K} \) are shown in Figure 2a. As anticipated from the theory, we find that both dynamic and nonlocal screening reduce the effective attraction between the electron and hole, but only the nonlocal screening results in a barrier to recombination.

The extrapolated binding energies are summarized in Table 1. Within the static screening approach, the exciton is hydrogenic, and the binding energy is given by \( \Delta E_B = \mu e^2 / 2(4\pi \varepsilon_r \varepsilon_0)^{\frac{1}{2}} \) where \( \mu \) is a reduced mass of the electron and hole. The large decrease in binding energy under dynamic screening reflects the polaronic effect. Since the experimentally derived value of \( \alpha \) is relatively small,49 we find the change to the binding energy is well approximated by first-order perturbation theory, yielding the known Fröhlich result, \( \Delta E_B^\text{fl} = 2\hbar k_o \omega / \alpha \).45 This reduction in the binding energy is consistent with recent Bethe–Salpeter calculations with perturbative electron–phonon interactions,23 but higher than experimental estimates.44 The reduction in the binding energy from the nonlocal screening is 12 meV, which is close to a prediction assuming hydrogenic 1s orbits, 17 meV.

In the low temperature limit, the classical lattice approximation employed to construct the nonlocal screening model is no longer valid. In this limit, quantization of the phonons can lead to hybridization and polaron formation. To estimate the quantum mechanical effect of phonons in this model, we have adopted a hybrid approach where we have added a single optical phonon as done in the dynamical approximation, to the effective potential description deduced from the classical lattice simulations. The dynamical mode is treated analogously as eq 15, while the effective potential is assumed to be constant at low temperatures and reflective of dynamic disorder. Treating both of these effects yields a binding energy of 20.8 meV in very good agreement with experiment.45

The bimolecular recombination rate, \( k_r \), is defined as the rate of change of the concentration of free charges,

\[
\frac{d\rho}{dt} = -k_r \rho_e \rho_h
\]

through the reaction \( e^- + h^+ \rightarrow \nu \), where \( \rho_e/h \) is the concentration of free electrons/holes. At typical working excitation densities for MAPbI\(_3\) based photovoltaics, radiative recombination is the limiting factor determining the charge carrier lifetime.52 We can evaluate \( k_r \) using Fermi’s golden rule for spontaneous emission, with an effective mass approximation.56–59 Within our quasiparticle path integral framework, the rate is given by a constant times a ratio of path partition functions,

\[
k_r = e^2 \sqrt{\varepsilon_0} \frac{E_{gap}^{\frac{3}{2}}}{2\pi e_0 \hbar^2 c^2 \mu Z_c} \leq \frac{Z_c}{Z_c} \leq \frac{Z_c}{Z_c}
\]

where \( E_{gap} = 1.64 \text{ eV} \) is the band gap energy for MAPbI\(_3\) and \( c \) is the speed of light. The subscript c on \( Z_c \) stands for combined path integral in which the two separate imaginary time paths are placed together to form a single, radiating path.
by linking same imaginary time slices. The ratio of path partition functions can be evaluated as

\[
\frac{Z_c}{Z} = 4\pi \int dR R^2 (e^{\Delta S/k_B T}) e^{-\beta\Delta F(R)}
\]

where we replace the ratio of partition functions by an exponential average at fixed \( R \) of the difference in path action \( \Delta S = S - S_c \) (SI eq S13).

The change in action is a reporter on the overlap between the electron and hole wave functions. The electron and hole radial probability distribution is described in Figure 2b, illustrating that the nonlocal screening effect increases the average distance between electron and hole. This is distinct from the effect of the dynamic screening, which is consistent with the small value of \( \alpha \), leaves the electronic distribution largely unaltered from the simple Wannier, static screening model. The decrease in electron hole overlap results in a nearly exponential decrease in \( k_i \) using the nonlocal screening theory relative to the static screening theory. For the nonlocal screening theory, we find \( k_i = 1.3 \times 10^{-10} \text{ cm}^3/s \), in excellent agreement with photoluminescence lifetime measurements.52

Assuming the only loss mechanism is due to bimolecular recombination, the lifetime of an electron hole pair is computable from \( \tau_r = 1/k_r \rho_r \). Summarized in Table 1 for \( \rho_r = 10^{17}/\text{cm}^3 \) are lifetime estimates using the different screening models. Both standard polaronic effects incorporated into the dynamic screening model as well as the nonlocal screening model increase the lifetimes of free charge carriers; however, the contribution of a nonlocal screening obtained from the MAPbI\(_3\) lattice is much more significant. The details on the bimolecular recombination rate calculations are in the SI section III.

By comparing these different simplified models that account for charge–lattice interactions, we find that the ability of the MAPbI\(_3\) lattice to nonlocally screen quasiparticles is sufficient to explain the particularly low exciton binding energy and recombination rate. Only this screening kernel in our unified Gaussian field theory formalism can suppress the electron–hole overlap enough to explain the anomalously long free carrier lifetime with weak lattice coupling strength. The particular nonlocal screening adopted here was deduced directly from explicit atomistic molecular dynamics simulations using a quasiparticle path integral framework. This framework is uniquely able to study the thermodynamics of this quasiparticle–lattice system at finite temperature.

The adoption of a spatially dependent screening is consistent with a growing literature pointing to the importance of dynamic disorder in lead halide perovskites.61–63 As it is the wave-vector-dependent dielectric susceptibility of the bulk ground state lattice that enters into the theory presented above, experimental measurements of such properties could afford a means of assessing potential materials with similarly long radiative lifetimes. Further, the barrier to bringing electrons and holes together we have discovered here undoubtedly has implications apart from offering an explanation of the particular high power conversion efficiencies of MAPbI\(_3\). For example, this repulsion may help explain observations of antibinding of biexcitons.77,78 The identification of a repulsive electron–hole interaction generated from the soft, polar modes of the perovskite lattice offers a key new design principle for photovoltaic materials. Searching for other systems that admit this type of interaction represents a promising new direction for materials discovery.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c00077.

Details of simulations, derivation of effective electron–hole interaction, and the bimolecular recombination rate with path integral framework, tables of potential parameters, figures of susceptibility plots, \( \Delta F \) vs temperature, ratio of partition functions vs number of beads, and schematic illustration of action paths (PDF)

AUTHOR INFORMATION

Corresponding Author

David T. Limmer — Department of Chemistry, University of California, Berkeley, California 94720, United States; Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States; Kavli Energy NanoScience Institute, Berkeley, California 94720, United States; orcid.org/0000-0002-2766-0688; Email: dlimmer@berkeley.edu

Authors

Yoonjae Park — Department of Chemistry, University of California, Berkeley, California 94720, United States
Amael Obliger — Department of Chemistry, University of California, Berkeley, California 94720, United States; Present Address: ISM, Université Bordeaux, CNRS, Talence, France

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the Physical Chemistry of Inorganic Nanostructures Program (No. KC3103). This research used resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility. Y.P. also acknowledges Kwanjeong Educational Foundation. D.T.L. acknowledges the Alfred P. Sloan Foundation.

REFERENCES

(1) de Quilettes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S. Impact of microstructure on local carrier lifetime in perovskite solar cells. Science 2015, 348, 683–686.

(2) Wehrenfennig, Christian; Eperon, Giles E.; Johnston, Michael B.; Snaith, Henry J.; Herz, Laura M.; Petrozza, Annamaria; Snaith, Henry J Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber. Science 2013, 342, 341–344.

https://doi.org/10.1021/acs.nanolett.2c00077

Nano Lett. XXXX, XXX, XXX–XXX
(4) Xing, Guichuan; Mathews, Nirajan; Lim, Swee Sien; Yantara, Natalia; Liu, Xinfeng; Sabha, Dharani; Grätzel, Michael; Mhaisalkar, Subodh; Sum, Tze Chien Low-temperature solution-processed wavelength-tunable perovskites for lasing. Nat. Mater. 2014, 13, 476–480.

(5) Sutton, Rebecca J.; Eperon, Giles E.; Miranda, Laura; Parrott, Elizabeth S.; Camino, Brett A.; Patel, Jay B.; Hörantner, Maximilian T.; Johnston, Michael B.; Haghhighipour, Amir Abbas; Moore, David T.; Snaith, Henry J. Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. Adv. Energy Mater. 2016, 6, 1502458.

(6) Lee, Michael M; Teuscher, Joël; Miyasaka, Tsutomu; Murakami, Takuro; Snaith, Henry J Efficient hybrid solar cells based on meso-structured organometal halide perovskites. Science 2012, 338, 643–647.

(7) Wang, He; Valkunas, Leonas; Cao, Thu; Whittaker-Brooks, Luisa; Fleming, Graham R Coulomb Screening and Coherent Phonon in Methylammonium Lead Iodide Perovskites. J. Phys. Chem. Lett. 2016, 7, 3284–3289.

(8) Zhu, X.-Y.; Podzorov, V. Charge Carriers in Hybrid Organic–Inorganic Lead Halide Perovskites Might Be Protected as Large Polaron. J. Phys. Chem. Lett. 2015, 6, 4758–4761.

(9) Chen, Y.; Yi, H. T.; Wu, X.; Haroldson, R.; Gartstein, Y. N.; Rodionov, Y. I.; Tikhonov, K. S.; Zakhidov, A.; Zhu, X. Y.; Podzorov, V. Extended carrier lifetimes and diffusion in hybrid perovskites revealed by Hall effect and photoluminescence measurements. Nat. Commun. 2016, 7, 12253.

(10) Cannelli, Oliviero; Nicola Colonna; Puppin, Michele; Rossi, Thomas C; Kinschel, Dominik; Leroy, Ludmila M D; Löffler, Janina; Budarz, James M.; March, Anne Marie; Doumy, Gilles; Al Haddad, Andre; Tu, Min-Feng; Kumagai, Yoshiaki; Waldo, Donald; Grigory Smolentsev; Krieg, Franziska; Boehme, Simon C; Kovalenko, Maksym V.; Chergui, Majed; Mancini, Giulia F Quantifying Photoinduced Polaronic Distortions in Inorganic Lead Halide Perovskite Nanocrystals. J. Am. Chem. Soc. 2021, 143, 9048–9059.

(11) Katan, Claudine; Molite, Aditya D.; Even, Jacky. Entropy in halide perovskites. Nat. Mater. 2018, 17, 377.

(12) Motta, Carlo; El-Mellouhi, Fedwa; Kais, Sabre; Tabet, Nouar; Alharbi, Fahhad; Sanvito, Stefano Revealing the role of organic cations in hybrid halide perovskite CH3NH3PbI3. Nat. Commun. 2015, 6, 7026.

(13) Brivio, Federico; Frost, Jarivist M.; Skelton, Jonathan M.; Jackson, Adam J.; Weber, Oliver J.; Weller, Mark T.; Gon
carb, S.; Bruschini, C.; Yallapragada, V. J.; Oron, D. Binding GW-BSE Study. J. Phys. Chem. Lett. 2019, 10, 6189–6196.

(14) Schlipf, Martin; Poncè, Samuel; Giustino, Feliciano Carrier Lifetimes and Polaronic Mass Enhancement in the Hybrid Halide Perovskite CH3NH3PbI3 from Multiphonon Fröhlich Coupling. Phys. Rev. Lett. 2018, 121, 086402.

(15) Zheng, F.; Wang, L.-w. Large polyarion formation and its effect on electron transport in hybrid perovskites. Energy Environ. Sci. 2019, 12, 1219–1230.

(16) Mayer, Matthew Z; Tan, Liang Z.; Egger, David A; Rappe, Andrew M; Reichman, David H. Low lattice and charge fluctuations control carrier dynamics in halide perovskites. Nano Lett. 2018, 18, 8041–8046.

(17) Menéndez-Proupin, E.; Beltrán Rios, Carlos L.; Wahón, P. Nonhydrogenic exciton spectrum in perovskite CH3NH3PbI3. Physica status solidi (RRL) - Rapid Research Letters 2015, 9, 559–563.

(18) Egger, David A; Bera, Achintya; Cahen, David; Hodes, Gary; Kirchhart, Thomas; Kronik, Leeor; Lovric, Robert; Rappe, Andrew M; Reichman, David R; Yafè, Omer What remains unexplained about the properties of halide perovskites? Adv. Mater. 2018, 30, 1800691.

(19) Filip, Marina R.; Haber, Jonah B.; Neaton, Jeffrey B. Phonon Screening of Excitons in Semiconductors: Halide Perovskites and Beyond. Phys. Rev. Lett. 2012, 107, 067401.

(20) Cho, Yeongsu; Berkelbach, Timothy C Optical properties of layered hybrid organic–inorganic halide perovskites: A tight-binding gw-bse study. J. Phys. Chem. Lett. 2019, 10, 6189–6196.

(21) Mattoni, Alessandro; Filippetti, Alessio; Caddeo, Claudia Modeling hybrid perovskites by molecular dynamics. J. Phys.: Condens. Matter 2017, 29, 043001.

(22) Mattoni, A.; Caddeo, C. Dielectric function of hybrid perovskites at finite temperature investigated by classical molecular dynamics. J. Chem. Phys. 2020, 152, 104705.

(23) Parrinello, Michele; Rahman, Aneesur Study of an f center in molten kcl. J. Chem. Phys. 1984, 80, 860–867.

(24) Schnitker, Jürgen; Rossky, Peter J. An electron−water pseudopotential for condensed phase simulation. J. Chem. Phys. 1987, 86, 3462–3470.

(25) Kuharški, Robert A; Bader, Joel S; Chandler, David; Sprik, Michiel; Klein, Michael I; Impy, Roger W Molecular model for aqueous ferrous−ferric electron transfer. J. Chem. Phys. 1988, 89, 3248–3257.

(26) Bischak, Connor G; Hetherington, Craig L; Wu, Hao; Aloni, Shaul; Frank O lateral, D; Limmer, David T; S Ginsberg, Naomi Origin of reversible photoinduced phase separation in hybrid perovskites. Nano Lett. 2017, 17, 1028−1033.

(27) Bischak, Connor G; Weng, Andrew B; Lin, Elbert; Limmer, David T; Young, Peidong S; Ginsberg, Naomi Tunable polaron distortions control the extent of halide demixing in lead halide perovskites. J. Phys. Chem. Lett. 2018, 9, 3998−4005.

(28) Limmer, D. T.; Ginsberg, N. S. Photoinduced phase separation in the lead halides is a polaronic effect. J. Chem. Phys. 2020, 152, 230901.

(29) Remsing, Richard C; Bates, Jefferson E Effective mass path integral simulations of quasiparticles in condensed phases. J. Chem. Phys. 2020, 153, 121104.

(30) Habershon, S.; Manolopoulos, D. E.; Markland, T. E.; Miller, T. F. Ring-polymer molecular dynamics: Quantum effects in chemical spectroscopy. J. Phys. Chem. Lett. 2013, 4, 387–413.

(31) Kumar, S; Rosenberg, J. M.; Bouzida, D.; Swendsen, R. H.; Kollman, P. A. THE weighted histogram analysis method for free-energy calculations on biomolecules. I. The method. J. Comput. Chem. 1992, 13, 1011.

(32) Einn, David Barrier to recombination of oppositely charged large polarons. J. Appl. Phys. 2018, 123, 055105.

(33) Lubin, G.; Yaniv, G.; Kazes, M.; Ulka, A. C.; Antolovic, I. M.; Burri, S.; Bruschini, C.; Charbon, E.; Yallapragada, V. J.; Oron, D. Resolving the controversy in biexciton binding energy of cesium lead halide perovskite nanocrystals through heralded single-particle spectroscopy. ACS Nano 2021, 15, 19581.

(34) Dana, Jayanta; Binyamin, Tal; Egar, Lioz; Ruhman, Sanford Unusually strong biexciton repulsion detected in quantum confined cs2pbbr3 nanocrystals with two and three pulse femtosecond spectroscopy. ACS Nano 2021, 15, 9039.

(35) Song, Xueyi; Chandler, David; Marcus, R. A. Gaussian field model of dielectric response dynamics. J. Chem. Phys. 1996, 100, 11954–11959.

(36) Cox, Stephen J; Mandapapu, Kranthi K; Geissler, Phillip L Quadrupole-mediated dielectric response and the charge-asymmetric solvation of ions in water. J. Phys. Chem. B 2021, 154, 244502.
(41) Li, Hao; Kardar, Mehran Fluctuation-induced forces between rough surfaces. Phys. Rev. Lett. 1991, 67, 3275.
(42) Brooks, Bernard R.; Janežič, Dušanka; Karplus, Martin Harmonic analysis of large systems. I. Methodology. J. Comput. Chem. 1995, 16, 1522–1542.
(43) Chandler, David Gaussian field model of fluids with an application to polymeric fluids. Phys. Rev. E 1993, 48, 2898.
(44) Reichman, David R; Voth, Gregory A Self-consistent harmonic theory of solvation in glassy systems: Classical solvation. J. Chem. Phys. 2000, 112, 3267–3279.
(45) Ferreira, A. C.; Paoai, Serge; Antoine, Létoublon; Ollivier, Jacques; Raymond, Stéphane; Bernard, Hehlen; Benoit, Rufflé; Cordier, Stéphane; Katan, Claudine; Even, Jacky; et al. Direct evidence of weakly dispersed and strongly anharmonic optical phonons in hybrid perovskites. Commun. Phys. 2020, 3, 48.
(46) Shih, Petra; Berkelbach, Timothy C. Anharmonic lattice dynamics from vibrational dynamical mean-field theory. arXiv:2109.00028 [cond-mat.mtrl-sci] 2021 (accessed Feb 1, 2022).
(47) Mozafari, Elham. Theoretical Description of the Electron-Lattice Interaction in Molecular and Magnetic Crystals; Linköping LiU-Tryck: Linköping, Sweden, 2016.
(48) Gerlach, B.; Luczak, F. Ground-state energy of an exciton-(LO) phonon system in two and three dimensions: General outline and three-dimensional case. Phys. Rev. B 1996, 54, 12841–12851.
(49) Sendner, Michael; Nayak, Pabitra K.; Egger, David A.; Beck, Sebastian; Müller, Christian; Edping, Bernd; Kowalsky, Wolfgang; Kronik, Leor; Snaith, Henry J. Annemarie Pucci, and Robert Lovričić, “Optical phonons in methylammonium lead halide perovskites and implications for charge transport. Materials Horizons 2016, 3, 613–620.
(50) Kornyshev, A. A. Nonlocal screening of ions in a structurized polar liquid—new aspects of solvent description in electrolyte theory. Electrochim. Acta 1981, 26, 1–20.
(51) Pollmann, J.; Büttner, H. Effective hamiltonians and bindings energies of wanner excitons in polar semiconductors. Phys. Rev. B 1977, 16, 4480.
(52) Herz, Laura M Charge-carrier dynamics in organic-inorganic metal halide perovskites. Annu. Rev. Phys. Chem. 2016, 67, 65–89.
(53) Deveese, J. T. Fröhlich polarons. lecture course including detailed theoretical derivations. arXiv:1012.4576 [cond-mat.other] 2015 (accessed Feb 1, 2022).
(54) Galkowski, Krzysztof; Mitioglu, Anatolie; Miyata, Atsuhiko; Plochocka, Paulina; Oliver, Portugalli; Eperon, G.; Gueze E; Wang, Jacob Tse-Wei; Stergiopoulos, Thomas; Stranks, Samuel D; Snaith, Henry J; et al. Determination of the exciton binding energy and effective masses for methylammonium and formamidinium lead tri-halide perovskite semiconductors. Energy Environ. Sci. 2016, 9, 962–970.
(55) D’Innocenzo, Valerieo; Granclini, Giulia; Marcelo, J.; Alcocer, P.; Srimath Kandada, Ajay Ram; Stranks, Samuel D.; Lee, Michael M.; Lanzani, Guglielmo; Snaith, Henry J.; Petrozza, Annamaria Excitons versus free charges in organo-lead tri-halide perovskites. Nat. Commun. 2014, 5, 3586.
(56) Peter, Y. Fundamentals of Semiconductor: Physics and Materials properties; Springer: New York, 2010.
(57) Hamaguchi, Chihiro. Basic Semiconductor Physics; Springer: New York, 2009.
(58) Sahin, Mehmet; Koç, Fatih A model for the recombination and radiative lifetime of trions and bieexcitons in spherically shaped semiconductor nanocrystals. Appl. Phys. Lett. 2013, 102, 183103.
(59) Fonoberov, Vladimir A.; Balandin, Alexander A. Excitonic properties of strained wurtzite and zinc-blende GaN/AlxGa1-xN quantum dots. J. Appl. Phys. 2003, 94, 7178–7186.
(60) Wimmer, Michael; Nair, S. V.; Shumway, J. Bieexciton recombination rates in self-assembled quantum dots. Phys. Rev. B 2006, 73, 165305.
(61) Leguy, Aurélien; Goñi, Alejandro R; Frost, Jarvist M; Skelton, Jonathan; Brivio, Federico; Rodriguez-Martinez, Xabier; Weber, Oliver J; Pallipurath, Anuradha; Alonso, M Isabel; Campoy-Quiles, Mariano; et al. Dynamic disorder, phonon lifetimes, and the assignment of modes to the vibrational spectra of methylammonium lead halide perovskites. Phys. Chem. Chem. Phys. 2016, 18, 27051–27066.
(62) Schilcher, Maximilian J; Robinson, Paul J; Abramovitch, David J; Tan, Liang Z; Rappe, Andrew M; Reichman, David R; Egger, David A The significance of polarons and dynamic disorder in halide perovskites. ACS Energy Letters 2021, 6, 2162–2173.
(63) Qian, Li Na.; Park, Yoonjae.; Guo, Peijun.; Gao, Mengyu.; Jin, Jianbo.; Huang, Jianmei.; Copper, Jason K.; Adam, Schwartzberg.; Schaller, Richard.; Limmer, David T. Vibrational relaxation dynamics in layered perovskite quantum wells. Proc. Natl. Acad. Sci. U. S. A. 2021, 118, e2104425118.
Supporting Information to “Nonlocal screening dictates the radiative lifetimes of excitations in the lead halide perovskites”

Yoonjae Park,¹ Amael Obliger,¹,* and David T. Limmer¹,²,³,⁴,†

¹Department of Chemistry, University of California, Berkeley
²Materials Science Division, Lawrence Berkeley National Laboratory
³Chemical Science Division, Lawrence Berkeley National Laboratory
⁴Kavli Energy NanoScience Institute, Berkeley, California, Berkeley

(Dated: February 25, 2022)

* Current Address: ISM, Univ. Bordeaux, CNRS, Talence, France
† dlimmer@berkeley.edu
I. SIMULATION DETAILS

A. MAPbI$_3$ lattice with electron and hole ring polymers

We consider MAPbI$_3$ lattice of 40×15×15 unit cells with electron and hole ring polymers. For the atomistic model of MAPbI$_3$ lattice, we adopt empirical force field from Ref [1]. Interactions between inorganic atoms (Pb, I) are described by Buckingham-Coulomb (BC) potential

$$U_{BC} = \sum_{i,j} A_{ij} e^{-r_{ij}/\rho_{ij}} - \frac{c_{ij}}{r_{ij}} + \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}}$$  \hspace{1cm} (S.1)

where $r_{ij}$ is the distance between $i$ and $j$ atoms, $\varepsilon_0$ is the vacuum electric permittivity, $q_i$ is the charge of atom $i$, and $A_{ij}$, $c_{ij}$, and $\rho_{ij}$ are parameters for BC potential. Other pairwise interactions are described by the sum of BC potential and Lennard-Jones (LJ) potential

$$U_{LJ} = \sum_{i,j} 4\varepsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} ight)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6$$  \hspace{1cm} (S.2)

with LJ parameter $\varepsilon_{ij}$ and $\sigma_{ij}$. Types and parameters for pairwise interactions can be found in Table S1 and Table S2. For electron and hole ring polymers, we used a quasiparticle path integral approach whose Hamiltonian obtained by discretizing the path action is given by

$$\mathcal{H}_{RP} = \sum_{j=1}^{n} \frac{m_e n}{2\beta^2 \hbar^2} (r_{e,j+1} - r_{e,j})^2 + \sum_{j=1}^{n} \frac{m_h n}{2\beta^2 \hbar^2} (r_{h,j+1} - r_{h,j})^2 - \sum_{j=1}^{n} \frac{e^2}{4\pi \varepsilon_0 n |r_{e,j} - r_{h,j}|}$$  \hspace{1cm} (S.3)

where $r_{e/h,j}$ is the position of the $j$th bead in electron/hole ring polymer, $n = 1000$ is the number of beads used in each ring polymer, $\beta = (k_B T)^{-1}$ is an inverse temperature, and $m_e/m_0 = m_h/m_0 = 0.2[2]$ are the band masses of electron and hole with the bare electron mass $m_0$. Pseudopotentials are given by truncated Coulomb potentials where $r^{-1}$ is replaced by $(\alpha_C + r^2)^{-1/2}$. The parameter $\alpha_C$ for electron-lattice, hole-lattice, and electron-hole interactions are chosen to recover the corresponding ionization energy, electron affinity, and the band gap of MAPbI$_3$ perovskite, summarized in Table S3 [3, 4].

Simulations are run in NVT ensemble with Langevin thermostat to control the temperature to 300K using timestep 0.5fs. In the free energy calculations using Umbrella sampling[5], we used 86 windows where the harmonic potentials $V(R) = 0.5 k_{sp}(R - R_{eq})^2$ are added to the distance between two centroids of ring polymers $R$ with the spring constant $k_{sp}$ ranging from 0.15 to 0.4 kcal/mol/Å$^2$. Prior to adding the ring polymers to the lattice, they are equilibrated for 500ps in NVT ensemble with Langevin thermostat at each window as is done in the staging algorithm[6]. We combine the equilibrated configuration of ring polymers with the lattice, run 200ps for equilibration purpose, and store trajectories in every 50fs for 700ps.

B. Electron and hole ring polymers under three types of screenings

Simulations with isolated electron and hole ring polymers are performed under each type of effective screening. For a static screening, the discretized Hamiltonian is given by Eq.S.3
with Coulomb interaction screened by dielectric constant \( \varepsilon_r = 6.1 \) \cite{7}. For the dynamic screening, Hamiltonian consists of two pieces, \( \mathcal{H}_{\text{dyn}} = \mathcal{H}_{\text{RP}} + \mathcal{H}_{\text{eff}} \). The second term is given by Eq. 15 with the factor of discretization \( n \),

\[
\mathcal{H}_{\text{eff}} = -\sum_{i,j \in \{e,h\}} \Gamma_{ij} \alpha \beta \frac{h^2 \omega^2}{n^2} \sqrt{\frac{\hbar}{8m_{ij} \omega}} \sum_{t=1}^{n} \sum_{s=1}^{n} e^{-\frac{\beta \omega}{n} |t-s|} \sqrt{\frac{1}{\mathbf{r}_{i,t} - \mathbf{r}_{j,s}}}
\]

(S.4)

where \( \mathbf{r}_{e/h,j} \) represents the position of the \( j^{\text{th}} \) bead in electron/hole ring polymer, \( \Gamma_{ij} = 1 \) if \( i = j \) and \( \Gamma_{ij} = -1 \) if \( i \neq j \), \( \alpha = 1.72 \) \cite{8} is Fröhlich coupling constant and \( \omega = 40 \text{cm}^{-1} \) \cite{8} is optical frequency of MAPbI\(_3\) perovskite with \( m_{eh} = \mu \). For the nonlocal screening, the last term in Eq.S.3 is replaced by the effective exciton interaction from empirical force field calculation shown in Fig.1c (black symbols), divided by the effective dielectric constant \( \varepsilon_r \) to account for the lack of explicit polarizability in the force field.

Simulations are run in NVT ensemble and Langevin thermostat with pseudopotential. For Umbrella sampling parameters, 65 windows are used with the spring constant \( k_{\text{sp}} = 0.2 \text{kcal/mol/Å}^2 \) and equilibrium distance \( R_{\text{eq}} \) starts from 3Å and is increased by 3Å at each window. In the first window, ring polymers are first equilibrated for 1ns with 1fs timestep and then trajectories are stored in every 500ps for 10ns. The last configuration of the previous window is taken to be the starting point of the next window. Simulations are performed using the LAMMPPS package\cite{9}.

II. DERIVATION OF AN EFFECTIVE ELECTRON-HOLE INTERACTION

Starting from the Gaussian approximated path action given by \( S_l + S_{\text{int}} \) from Eq.7 and Eq.8, its Fourier transform becomes

\[
\hat{S}_l + \hat{S}_{\text{int}} = \frac{1}{2} \int_k \int_\omega \chi_{k,\omega}^{-1} \mathbf{u}_{k,\omega}\mathbf{u}_{k,\omega}^* + \int_k \int_{\tau=0}^{\beta h} \int_\omega \mathbf{u}_{k,\omega} e^{-i\omega\tau} \lambda \frac{e^{i \mathbf{k} \cdot \mathbf{r}_{e,\tau}} - e^{i \mathbf{k} \cdot \mathbf{r}_{h,\tau}}}{k}
\]

(S.5)

where a Fröhlich-type coupling constant \( \lambda \) is defined as

\[
\lambda = -i \hbar \omega \left( \frac{4 \pi \alpha}{V} \right)^\frac{1}{2} \left( \frac{\hbar}{2m\omega} \right)^\frac{1}{2} \left( \frac{2\omega}{\hbar} \right)^\frac{1}{2}
\]

(S.6)

with dimensionless coupling constant \( \alpha \)\cite{10}. Using the fact that the Gaussian integral of the form of \( e^{-x^2/2a^2+ax} \) with respect to \( x \) produces the term of \( e^{\sigma^2|x|^2/2} \) gives the effective path action defined in Eq.9 as

\[
S_{\text{eff}} = -\frac{1}{2} \int_k \int_\omega \chi_{k,\omega} \left| \int_{\tau=0}^{\beta h} e^{-i\omega\tau} \lambda \frac{e^{i \mathbf{k} \cdot \mathbf{r}_{e,\tau}} - e^{i \mathbf{k} \cdot \mathbf{r}_{h,\tau}}}{k} \right|^2
\]

\[
= -\frac{1}{2} \int_{\tau=0}^{\beta h} \int_{\tau'=0}^{\beta h} \int_k \int_\omega \chi_{k,\omega} e^{-i\omega(\tau-\tau')} \left| \lambda \right|^2 \frac{\left| e^{i \mathbf{k} \cdot \mathbf{r}_{e,\tau}} - e^{i \mathbf{k} \cdot \mathbf{r}_{h,\tau}} \right|^2}{k^2}
\]

(S.7)

\[
= -\frac{1}{2} \int_{\tau=0}^{\beta h} \int_{\tau'=0}^{\beta h} \int_k \chi_{k,\tau-\tau'} \left| \lambda \right|^2 \frac{\left| e^{i \mathbf{k} \cdot \mathbf{r}_{e,\tau}} - e^{i \mathbf{k} \cdot \mathbf{r}_{h,\tau}} \right|^2}{k^2}
\]
where inverse Fourier representation of $\chi_{k,\omega}$ is used in the third line, which can be reduced to Eq.10 in the compact form.

In the classical limit, taking $\chi_{k,\tau} = \chi_k \delta(\tau)$ removes the $\tau$ dependence in the effective path action and gives an effective electron-hole interaction as Eq.11. We perform explicit MD simulations of MAPbI$_3$ lattice without electron and hole quasiparticles and compare $\chi(r)$ in real space where an analytic expression can be derived from the inverse Fourier transform using residue theorem with $\gamma$ and $\delta$ defined in Eq.S.10.

$$\chi(r) = \frac{\chi_0}{4\pi r} \frac{(\gamma^2 + \delta^2)^2}{4\gamma\delta} e^{-r\delta} \sin[r\gamma] \tag{S.8}$$

Fig.S1 shows $\chi(r)$ from MD simulation (black solid line) and from Eq.S.8 (red dotted line) where the reasonable agreement shows the validity of the functional form of $\chi_k$ given by Eq.12. Using Eq.11 and 12, performing inverse Fourier transform with residue theorem gives

$$V_{\text{eff}}(r) = -\frac{e^2}{4\pi \varepsilon_0 \hbar} \left[ \frac{1}{\varepsilon_{\infty}} + \frac{1}{\varepsilon^*} - \frac{e^{-r\delta}}{2\varepsilon^*} \left( \cos[r\gamma] - \frac{\gamma^2 - \delta^2}{2\gamma\delta} \sin[r\gamma] \right) \right] \tag{S.9}$$

where parameters, $\gamma$ and $\delta$ are defined as follows.

$$\frac{1}{\varepsilon^*} = \frac{\lambda_0 |\lambda|^2 \varepsilon_0}{e^2} \quad , \quad \gamma = \sqrt{\frac{1}{2l_v l_c} + \frac{1}{4l_c^2}} \quad , \quad \delta = \sqrt{\frac{1}{2l_v l_c} - \frac{1}{4l_c^2}} \tag{S.10}$$

Since $\gamma \gg \delta$, the relation, $a \sin \theta - b \cos \theta = \sqrt{a^2 + b^2} \sin[\theta - \arctan(b/a)]$, simplifies the effective electron-hole interaction as given in Eq.13.

### III. BIMOLECULAR RECOMBINATION RATE WITH PATH INTEGRAL

The bimolecular recombination rate derived from Fermi’s golden rule under effective mass approximation can be computed from the ratio of partition functions[11–15]

$$k_{\tau} = \frac{e^2 \sqrt{\varepsilon_{\infty}} E_{\text{gap}}^2}{2\pi \varepsilon_0 \hbar^2 c^3 \mu} \frac{Z_c}{Z} \tag{S.11}$$

where $e$ is the charge of an electron, $\varepsilon_0$ is vacuum electric permittivity, $\varepsilon_{\infty}$ is the dielectric constant related to the index of refraction, $\hbar$ is Planck’s constant, $c$ is the speed of light, $\mu$ is the reduced mass of electron and hole, and $E_{\text{gap}} = 1.64$eV is the band gap energy for MAPbI$_3$ perovskite. In the path integral framework, $Z$ indicates the path for two separate (electron and hole) quasiparticles and $Z_c$ stands for the combined path where electron and hole paths are combined forming a radiating path by linking the same imaginary time slices. $Z_c$ can be rewritten in terms of $Z$ and the difference in path action $\Delta S = S - S_c$,

$$Z_c = \int D[r_e, r_h] e^{-S_c + S - S} \frac{Z}{Z} = Z \int D[r_e, r_h] \frac{e^{-S}}{Z} e^{-S_c + S} = Z \langle e^{\Delta S} \rangle \tag{S.12}$$

where $S$ and $S_c$ are the path actions of two separate and combined paths. The change in path action $\Delta S$ is give by

$$\Delta S = \int_{\tau=0}^{\beta} \frac{m_e \dot{r}_{e,\tau}^2}{2} + \frac{m_h \dot{r}_{h,\tau}^2}{2} + \frac{\mu \dot{r}_{c,\tau}^2}{2}$$
where \( \mathbf{r}_c \) is a combined path integral where the two paths are shown in Figs. S3b and c. With the conditional probability representation, the ratio of partition functions becomes

\[
\frac{Z_c}{Z} = \langle e^{\Delta S} \rangle = \int d\Delta S \ P(\Delta S) \ e^{\Delta S} = \int d\Delta S \left[ 4\pi \int dR \ R^2 P(\Delta S|R) \ P(R) \right] e^{\Delta S} = 4\pi \int dR \ R^2 \int d\Delta S \ P(\Delta S|R) \ e^{\Delta S} P(R) = 4\pi \int dR \ R^2 \langle e^{\Delta S} \rangle_R P(R)
\]

(S.13)

where \( \langle e^{\Delta S} \rangle_R \) indicates the value of \( \langle e^{\Delta S} \rangle \) given \( R \) and \( P(R) \) can be computed from the free energy. Plugging Eq.S.13 into Eq.S.11 results in Eq.19. Shown in Fig.S3a is the ratio of partition function with various number of beads. Since the error of Trotter factorization in path integral approach scales by \( n^{-2} \), we compute the carrier lifetime using the value extrapolated to \( n \to \infty \).

[1] Alessandro Mattoni, Alessio Filippetti, and Claudia Caddeo, “Modeling hybrid perovskites by molecular dynamics,” Journal of Physics: Condensed Matter 29, 043001 (2016).
[2] Yeongsu Cho and Timothy C Berkelbach, “Optical Properties of Layered Hybrid Organic-Inorganic Halide Perovskites: A Tight-Binding GW-BSE Study,” The Journal of Physical Chemistry Letters 10, 6189–6196 (2019).
[3] Mehmet Sahin and Fatih Ko, “A model for the recombination and radiative lifetime of trions and biexcitons in spherically shaped semiconductor nanocrystals,” Applied Physics Letters 102, 183103 (2013), 1305.0906.
[4] Jürgen Schnitker and Peter J Rossky, “An electron-water pseudopotential for condensed phase simulation,” The Journal of Chemical Physics 86, 3462–3470 (1987).
[5] Michael R. Shirts and John D. Chodera, “Statistically optimal analysis of samples from multiple equilibrium states,” The Journal of Chemical Physics 129, 124105 (2008), 0801.1426.
[6] Michiel Sprik, Michael L. Klein, and David Chandler, “Staging: A sampling technique for the Monte Carlo evaluation of path integrals,” Physical Review B 31, 4234–4244 (1985).
[7] Teruya Ishihara, Jun Takahashi, and Takenari Goto, “Optical properties due to electronic transitions in two-dimensional semiconductors (CnH2n+1NH3)2PbI4,” Physical Review B 42, 11099–11107 (1990).
[8] Michael Sendner, Pabitra K. Nayak, David A. Egger, Sebastian Beck, Christian Müller, Bernd Epding, Wolfgang Kowalsky, Lecor Kronik, Henry J. Snaith, Annemarie Pucci, and Robert Lavrini, “Optical phonons in methylammonium lead halide perovskites and implications for charge transport,” Materials Horizons 3, 613–620 (2016), 1607.08541.
[9] S. Plimpton, “Fast Parallel Algorithms for Short-Range Molecular Dynamics.” J Comp Phys 117, 1–19 (1995).
[10] Elham Mozafari, Theoretical Description of the Electron-Lattice Interaction in Molecular and Magnetic Crystals (Linkping LiU-Tryck, Linkping, Sweden, 2016).
[11] Michael Wimmer, S. V. Nair, and J. Shumway, “Biexciton recombination rates in self-assembled quantum dots,” Physical Review B 73 (2006), 10.1103/physrevb.73.165305, cond-mat/0512603.

[12] Peter Y. Yu and Manuel Cardona, Fundamentals of Semiconductor: Physics and Materials properties (Springer, New York, 2010).

[13] Chihiro Hamaguchi, Basic Semiconductor Physics (Springer, New York, 2009).

[14] Mehmet Sahin and Fatih Ko, “A model for the recombination and radiative lifetime of trions and biexcitons in spherically shaped semiconductor nanocrystals,” Applied Physics Letters 102, 183103 (2013), 1305.0906.

[15] Vladimir A. Fonoberov and Alexander A. Balandin, “Excitonic properties of strained wurtzite and zinc-blende GaN/AlxGa1xN quantum dots,” Journal of Applied Physics 94, 7178–7186 (2003), cond-mat/0310363.
TABLE S1. Parameters for Buckingham potential (Eq. S.1).

| $i$ | $j$ | $A_{ij}$ (kcal/mol) | $\rho_{ij}$ (Å) | $c_{ij}$ (kcal/mol/Å$^6$) |
|-----|-----|---------------------|------------------|--------------------------|
| Pb  | Pb  | 70359906.629702     | 0.131258         | 0.0000                   |
| Pb  | I   | 103496.133010       | 0.321737         | 0.0000                   |
| Pb  | C/N | 32690390.937995     | 0.150947         | 0.0000                   |
| I   | I   | 24274.905590        | 0.482217         | 696.949542               |
| I   | C/N | 112936.714213       | 0.342426         | 0.0000                   |

TABLE S2. Parameters for Lennard-Jones potential (Eq. S.2). The hydrogen atoms in ammonium NH$_3^+$ group are indicated by H$_n$.

| $i$ | $j$ | $\varepsilon_{ij}$ (kcal/mol) | $\sigma_{ij}$ (Å) |
|-----|-----|-------------------------------|-------------------|
| Pb  | H$_n$| 0.0140                        | 2.26454           |
| Pb  | H   | 0.0140                        | 2.70999           |
| I   | H$_n$| 0.0574                        | 2.750             |
| I   | H   | 0.0574                        | 3.100             |
| C   | C   | 0.1094                        | 3.39970           |
| C   | N   | 0.1364                        | 3.32480           |
| C   | H$_n$| 0.0414                        | 2.23440           |
| C   | H   | 0.0414                        | 2.67980           |
| N   | N   | 0.1700                        | 3.250             |
| N   | H$_n$| 0.0517                        | 2.15950           |
| N   | H   | 0.0517                        | 1.0690            |
| H$_n$| H$_n$| 0.0157                        | 1.06910           |
| H$_n$| H   | 0.0157                        | 1.51450           |
| H   | H   | 0.0157                        | 1.960             |

TABLE S3. Pseudopotential parameter $\alpha_C$ where $b_{e(h)}$ indicates the bead in the electron(hole) ring polymer.

| $\alpha_C$ | Pb | I | $b_e$ | $b_h$ |
|------------|----|---|-------|-------|
| $b_e$      | 3.67| 0.005| -     | 2.072 |
| $b_h$      | 0.005| 22.152| 2.072 | -     |
FIG. S1. Susceptibility $\chi(r)$ from explicit MD simulation (black solid line) and from Eq.S.8 (red dotted line). Gray dotted line is the guideline for 0.
FIG. S2. The difference in free energy $\Delta F$ as a function of temperature under static screening (circles), dynamic screening (diamonds), nonlocal screening (triangles), and nonlocal screening combined with polaronic effect (squares). Solid lines are corresponding fitted lines.
FIG. S3. (a) Ratio of partition function with various number of beads. Dotted lines are linear fittings under each type of screening. Schematic picture of (b) two separate paths $S$ and (c) combined path $S_c$. 