Breakdown of the Born–Oppenheimer Approximation in Strongly Correlated Polaron Systems: Implications for Non-Adiabatic Charge Transport in Two-Dimensional Perovskite Heterostructures

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Abstract. The Born–Oppenheimer approximation (BOA) has long served as a foundational pillar in condensed matter and molecular physics, yet its validity in strongly correlated polaron systems remains insufficiently scrutinized. This study systematically examines the breakdown regimes of the BOA within two-dimensional hybrid organic–inorganic perovskite heterostructures by employing a combination of many-body perturbation theory, non-adiabatic path-integral molecular dynamics, and time-resolved angle-resolved photoemission spectroscopy (tr-ARPES). We identify critical electron–phonon coupling thresholds beyond which adiabatic decoupling fails catastrophically, producing anomalous charge transport signatures including negative differential mobility and sub-Drude optical conductivity. Our findings challenge prevailing models of polaron hopping and provide a revised non-adiabatic Hamiltonian framework that quantitatively reproduces experimental observations, with significant implications for next-generation perovskite-based optoelectronic device engineering.

Keywords: Born–Oppenheimer approximation breakdown, non-adiabatic charge transport, strongly correlated polaron systems, two-dimensional perovskite heterostructures, electron–phonon coupling, many-body perturbation theory, time-resolved ARPES, non-adiabatic path-integral molecular dynamics, sub-Drude optical conductivity

Introduction

The Born–Oppenheimer approximation (BOA), first formulated in 1927, posits that the motion of atomic nuclei and electrons in a quantum mechanical system can be decoupled due to the vast disparity in their respective masses. For nearly a century, this approximation has underpinned theoretical frameworks across molecular physics, quantum chemistry, and condensed matter physics, enabling tractable solutions to otherwise intractable many-body Hamiltonians. However, as the frontier of materials science pushes deeper into the domain of strongly correlated quantum systems — particularly those exhibiting large polaronic effects and competing instabilities — the fundamental assumptions of the BOA are being placed under unprecedented scrutiny. In two-dimensional hybrid organic–inorganic perovskite (2D-HOIP) heterostructures, which have risen to extraordinary prominence in photovoltaic, light-emitting, and neuromorphic device research between 2022 and 2025, the coexistence of soft phonon modes, large dielectric polarizability, and strong spin–orbit coupling creates a uniquely hostile environment for adiabatic decoupling. Experimental observations of anomalous Hall mobilities, non-Drude terahertz conductivity spectra, and temperature-independent carrier lifetimes in these systems have increasingly resisted explanation within the standard Fröhlich polaron model, suggesting that non-adiabatic electron–phonon interactions play a far more decisive role than previously acknowledged. Despite several computational and spectroscopic studies documenting deviations from adiabatic behavior, a coherent theoretical framework quantitatively delineating the BOA breakdown regimes in 2D-HOIP heterostructures has remained absent from the literature. The urgency of resolving this theoretical deficit is amplified by the accelerating deployment of perovskite-based optoelectronics at the industrial scale. Misattribution of transport anomalies to extrinsic defect scattering — rather than to intrinsic non-adiabatic polaron dynamics — has systematically misdirected passivation strategies and interface engineering efforts, constraining device efficiencies below thermodynamic limits. As the community targets perovskite tandem solar cell efficiencies exceeding 35% and sub-nanosecond electroluminescent switching speeds, the mechanistic accuracy of the underlying transport physics becomes not merely academically significant but technologically imperative. The present work addresses this gap through a multi-pronged theoretical and experimental approach. We develop a generalized non-adiabatic Hamiltonian that incorporates dynamic electron–phonon vertex corrections beyond the Migdal approximation, parameterized against high-resolution tr-ARPES datasets and benchmarked via non-adiabatic path-integral molecular dynamics simulations. Section 2 outlines the theoretical formalism and identifies the dimensionless coupling parameters governing BOA validity. Section 3 presents the computational methodology and experimental characterization protocols. Section 4 reports the principal results, including the identification of catastrophic adiabatic decoupling thresholds and the emergence of negative differential mobility regimes. Section 5 discusses the implications for polaron hopping models and proposes a revised transport taxonomy. Section 6 concludes with prospective directions for non-adiabatic device physics.

References

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