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Machine Learning for Simulating Photophysics in Nanomaterials

by

Kailai Lin

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Eran Rabani, Chair

Professor David Limmer

Professor Feng Wang

Spring 2026

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Abstract

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Professor Eran Rabani, Chair

Semiconductor nanocrystals exhibit size-, shape-, and composition-dependent electronic and optical properties governed by quantum confinement. Predictive computational modeling of these effects remains challenging because accurate first-principles excited-state methods such as GW/BSE scale too steeply for nanocrystals containing hundreds to thousands of atoms, while traditional semi-empirical approaches sometimes struggle to achieve the flexibility and transferability needed across diverse semiconductor materials and alloy compositions. At the same time, despite major advances in machine learning for ground-state materials modeling, its application to excited-state properties, electron-phonon interactions, optical response, and charge carrier dynamics of large nanomaterial systems remains limited.

This dissertation addresses this challenge through the development of DeepPseudopot, a machine-learned atomistic semi-empirical pseudopotential framework for nanomaterials. By combining a neural-network description of local screened pseudopotentials with physically motivated nonlocal and spin-orbit terms, DeepPseudopot retains the physical grounding of pseudopotential theory while extending its flexibility and predictive capability. Trained on high-level theory reference data from a compact set of bulk system calculations, the model enables accurate atomistic predictions of electronic structure across a broad range of semiconductors. Importantly, it generalizes beyond the materials and environments explicitly included in training, allowing predictive treatment of unseen crystal phases, continuous alloy compositions, chemically distinct systems, and nanostructures of experimentally relevant sizes without retraining.

Using this framework, this dissertation investigates the excited-state properties and photophysics of colloidal III-V nanocrystals newly accessible through recent synthetic advances. In close collaboration with experiment, DeepPseudopot is applied to GaAs quantum dots to predict excitonic fine structure, radiative lifetimes, Stokes shifts, and ensemble optical properties in quantitative agreement with measurements. The framework is further extended to describe single-nanocrystal photoluminescence spectral lineshape, providing a microscopic

interpretation of fluorescence line narrowing and photoluminescence excitation spectra. It is then used to reveal how alloying in ternary III-V quantum dots, including $\text{In}_{1-x}\text{Ga}_x\text{P}$ and $\text{GaP}_{1-x}\text{As}_x$, continuously reshapes band-edge wavefunction character and symmetry, thereby tuning oscillator strengths and photoluminescence quantum yield. Combined with open quantum system dynamics simulation and two-dimensional electronic spectroscopy, these atomistic calculations further clarify how alloying controls ultrafast hot-exciton relaxation pathways and electronic coherences. Together, these results highlight the need for a unified atomistic description of nanocrystal photophysics and establish a foundation for data-driven design of semiconductor nanomaterials.

To Mom and Dad,
on whose shoulders I could reach for the stars.

“Everything we love about civilization is a product of intelligence, so amplifying our human intelligence with artificial intelligence has the potential of helping civilization flourish like never before, as long as we manage to keep the technology beneficial.”

— Max Tegmark

Life 3.0: Being Human in the Age of Artificial Intelligence (2017)

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Chapter 1

Introduction

1.1 Machine learning in computational nanoscience

Computational materials science plays a central role in modern scientific discovery and novel materials design, impacting a wide range of applications and industries including semiconductors, [1] optical materials, [2] photovoltaics, [3] batteries, [4] thermoelectrics, [5] drug discoveries, [6] and quantum technologies. [7] The ability to compute materials properties efficiently *in silico* enables high-throughput screening providing insights that complement and potentially guide experiments. As the scope and complexity of materials challenges continue to expand, there is a growing demand for computational approaches that are both accurate and scalable.

The past decade has seen a paradigm shift toward data-driven approaches in materials science, catalyzed by the Materials Genome Initiative [8] and the establishment of large-scale open computational databases such as the Materials Project, [9] AFLOW, [10] NOMAD, [11] and JARVIS. [12] These repositories, built from millions of density functional theory calculations, have provided the foundation for machine learning (ML) to emerge as a powerful accelerator for materials simulation, enabling predictive models trained on vast computational or experimental data to bypass costly first-principles calculations. [13, 14] ML has since achieved notable successes across diverse materials domains. In heterogeneous catalysis, the Open Catalyst Project and its follow-up versions have trained large-scale graph neural network (GNN) models on DFT relaxation datasets to predict the solid-ligand adsorption configuration and accelerate the discovery of metal catalysts for renewable energy applications. [15–17] In energy storage, ML-guided screening has accelerated the identification of novel electrolyte formulations and electrode materials for lithium-ion and solid-state batteries. [18] In drug discovery, generative models and molecular property predictors have reshaped virtual screening and lead optimization pipelines. [19] More broadly, ML models for direct property prediction — including crystal graph neural networks for formation energies and band gaps, [20–22] and universal foundation models trained across the periodic table [23] — have demonstrated that data-driven surrogates can achieve useful accuracy for

rapid materials screening without requiring system-specific retraining.

Among the most impactful applications of ML in atomistic simulation are machine-learned interatomic potentials (MLIPs). ML models that leverage architectures such as multi-layer feed-forward neural networks, kernel methods, and graph neural networks combine flexible function approximators with physically motivated symmetry-preserving model architectures to learn representations of atomic interactions with near *ab initio* accuracy at a fraction of the computational cost. [24–31] These models approximate the Born–Oppenheimer potential energy surface and enable efficient, transferable predictions of total energies and atomic forces. [32–38]

Beyond interatomic potentials, machine learning has also been integrated into electronic structure simulations through the learning of diverse representations, including mean-field Hamiltonians, [39–41] electron densities, [42, 43] many-body Green’s functions, [44] transferable pseudopotentials, [45–47] and tight-binding models. [48, 49] These developments have enabled efficient electronic structure simulations for large and complex systems that are otherwise inaccessible to traditional first-principles methods. [50] In this dissertation, we contribute to this direction by developing machine-learned models of semi-empirical pseudopotential Hamiltonians that enable scalable prediction of excited-state, optical, and charge carrier dynamic properties for semiconductor nanostructures.

Despite rapid progress, machine learning for science remains fundamentally constrained by the quality, diversity, and physical fidelity of the training data. In computational materials science, meaningful advances therefore require continued development of traditional simulation methods that capture increasingly complex physical processes beyond standard electronic structure or classical descriptions of nuclear dynamics. Improvements in the treatment of electronic correlation, many-body effects, electronic-nuclear coupling, and vibronic dynamics not only deepen physical understanding, but also provide high-quality training data that will enable robust ML models. Conversely, ML offers a powerful route to overcome some long-standing limitations of conventional simulations, particularly the trade-off between accuracy and computational cost. By learning effective representations of complex quantum interactions, modern ML models can extend high accuracy to larger systems and longer timescales. MLIPs exemplify this synergy, delivering near *ab initio* accuracy for energies and forces at costs comparable to classical molecular dynamics. Together, advances in machine learning and physics-based simulation form a mutually reinforcing framework that is reshaping computational materials science. This dissertation contributes to *both directions* of this interplay, developing physically informed machine-learning models while advancing the underlying simulation methods that support them. We employ many-body perturbation theory to generate high-fidelity reference data that encode quasiparticle and excitonic effects beyond DFT. Meanwhile, the physically informed machine-learning model we built, once trained, helps extend these costly computational methods to semiconductor nanostructures of experimentally relevant sizes and compositional complexity.

Among the systems where this interplay is most consequential, semiconductor nanocryst-

tals represent a particularly challenging yet scientifically rich regime. Due to their finite size, nanocrystals exhibit strong size-, shape-, and composition-dependent properties that differ qualitatively from those of the corresponding bulk materials. [51, 52] Quantum confinement discretizes the electronic states, modifies the selection rules for optical transitions, and enhances excitonic effects, giving rise to tunable photoluminescence, size-dependent band gaps, and modified carrier dynamics that underpin applications in displays, lasers, photodetectors, and solar cells. [53] These materials also show promise for emerging applications in quantum information science, [54] high-performance photonics, [55] and photocatalysis. [56] From a computational perspective, nanocrystals pose demanding requirements: their large system sizes—typically hundreds to thousands of atoms—necessitate favorable computational scaling, while their optoelectronic properties require levels of theoretical accuracy that go beyond standard density functional theory. [51, 57, 58] Many relevant properties of nano-materials arise from photophysical processes, including excited-state dynamics, [59] radiative recombination, [60] nonradiative electron-phonon relaxation, [61, 62] and defect- or surface-mediated decay pathways. [63] These phenomena involve coupled electronic and nuclear degrees of freedom and extend beyond the scope of conventional ground-state electronic structure methods or classical molecular dynamics. Accurate modeling of nanocrystal photophysics thus requires unified theoretical frameworks capable of describing electronic structure, lattice dynamics, and nonadiabatic effects on equal footing.

Although machine learning has achieved notable success in ground-state materials modeling, its application to the excited-state and dynamical properties of nanomaterials remains comparatively underexplored. Most importantly, the photophysical phenomena that govern nanocrystal performance—excitonic fine structure, radiative and nonradiative recombination rates, exciton-phonon coupling strengths, and hot-carrier relaxation dynamics—involve inherently many-body, coupled electronic-nuclear processes for which scalable, high-fidelity reference methods are scarce and standardized training datasets do not yet exist. The large system sizes of experimentally relevant nanocrystals (hundreds to thousands of atoms) further compound this gap: first-principles excited-state methods such as many-body perturbation theory scale steeply with system size, making brute-force dataset generation impractical. As a result, nanomaterials represent an ideal yet largely untapped testbed for the development of new ML-enabled simulation frameworks that integrate physically motivated modeling with data-driven learning to capture complex photophysical behavior at realistic length and time scales.

1.2 Colloidal III-V nanocrystals: from synthesis to photophysics

Realizing and validating the potential of data-driven modeling of nanomaterials requires experimental access to high-quality nanocrystals across diverse material families. Over the past two decades, colloidal synthesis has achieved nearly perfect control over size, shape, and

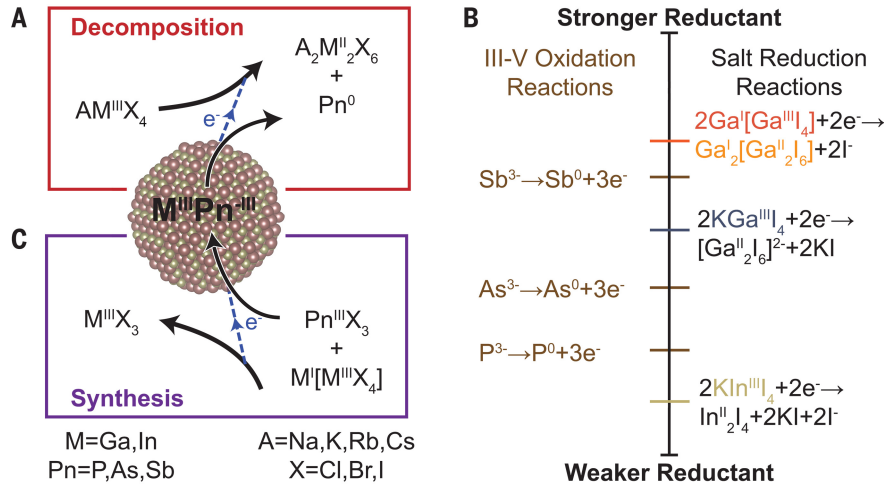


Figure 1.1: Molten salt redox chemistry. (A) The relation between molten salt redox chemistry and III-V NCs that controls the NCs' chemical stability. (B) Qualitative electrochemical scale for key reactions governing the stability of the pnictide component of the III-V NCs compared with redox reactions of III-halide molten salt. (C) Molten salt redox chemistry for precursor activation during NC synthesis.

physical properties for several well-established semiconductor nanocrystal families, including II-VI semiconductors (CdSe, CdS, ZnSe), [64, 65] IV-VI semiconductors (PbS, PbSe), [66] lead halide perovskites, [67] and indium pnictides (InP, InAs). [68–70] Successful commercial adoption of colloidal quantum dots has demonstrated that solution-phase synthesis, which is inherently scalable, can be competitive in material quality with much more expensive epitaxial growth techniques such as molecular beam epitaxy and chemical vapor deposition. [71] However, a critical omission has persisted: the colloidal synthesis of high-quality gallium-containing III-V semiconductors, including GaAs, GaP, and related ternary alloys. In their bulk form, these materials underpin the highest-efficiency multijunction solar cells, high-brightness light-emitting diodes, semiconductor lasers, and high-speed electronic devices. [72] Quantum-confined GaAs and GaP nanocrystals are particularly attractive because they access band gaps in the visible and near-infrared spectral regions — including the blue-emitting window that is of interest for display and short-wavelength photonic applications — thereby extending the spectral reach of the colloidal nanocrystal toolkit beyond what is available from established II-VI and IV-VI platforms. Numerous attempts to synthesize colloidal gallium pnictides using conventional organic solution routes have yielded materials of poor crystalline quality that lack band-edge emission, [73–75] leaving the nanocrystal regime of these technologically important semiconductors largely unexplored.

The central obstacle to colloidal gallium pnictide synthesis lies in the extreme reactivity of molecular Ga^{III} precursors and the high crystallization temperatures required for defect-free

III-V lattices. In conventional colloidal synthesis, nanocrystals are typically grown at the highest temperatures tolerated by organic solvents and ligands. [55, 64] Together with the known degradation of GaAs grown at low temperatures by MBE, [76, 77] these observations suggest that successful colloidal synthesis of gallium pnictides may require temperatures incompatible with standard organic media. Furthermore, the much higher Lewis acidity of molecular Ga^{III} species compared with In^{III} or Cd^{II} species promotes side reactions of gallium precursors with organic molecules. Molten inorganic salts provide a route to overcome these limitations. Compared to organic solvents, molten salts offer substantially greater thermal stability, improved chemical robustness, and wider electrochemical windows (Fig. 1.1). [78] It was first demonstrated that presynthesized InP and InAs nanocrystals can undergo partial cation exchange in gallium-containing molten salts at temperatures between 350 and 500 °C to form $\text{In}_{1-x}\text{Ga}_x\text{P}$ and $\text{In}_{1-x}\text{Ga}_x\text{As}$ nanocrystals exhibiting strong photoluminescence. [79] These results established molten salts as viable reaction media for accessing high-quality gallium-containing III-V nanocrystals. Subsequently, the redox chemistry of molten salts was leveraged to directly nucleate and grow monodisperse GaAs, GaP, $\text{GaP}_{1-y}\text{As}_y$, and $\text{GaAs}_{1-y}\text{Sb}_y$ nanocrystals, with shape control achieved through molten-salt “surfactant” additives. Most notably, size-dependent band-edge photoluminescence was demonstrated for colloidal GaAs quantum dots for the first time (Fig. 1.2).

Beyond enabling access to previously inaccessible binary III-V nanocrystals, the molten-salt platform opens a particularly compelling avenue: the synthesis of ternary alloyed nanocrystals with continuously tunable composition. In bulk semiconductors, electronic transitions must conserve both energy and crystal momentum, dividing materials into two distinct families: direct-gap semiconductors, where the valence-band maximum and conduction-band minimum occur at the same point in the Brillouin zone, and indirect-gap semiconductors, where they do not. [81] This distinction has profound consequences for optoelectronic behavior. Direct-gap semiconductors such as CdSe and InP exhibit strong dipole-allowed interband transitions, high luminescence efficiency with fast nanosecond radiative lifetimes, [82, 83] and state-filling-induced transient optical bleaching upon photoexcitation. [84, 85] By contrast, indirect-gap materials such as silicon and germanium require phonon-assisted processes for band-edge absorption and emission, resulting in weak absorption onsets, long microsecond radiative lifetimes, [86] and the absence of distinct excitonic bleach features. [87] Quantum confinement partially relaxes momentum conservation through spatial localization of carrier wavefunctions, and indeed low-temperature measurements on silicon nanocrystals have revealed zero-phonon emission lines indicative of weak Γ -X mixing [88, 89], yet silicon remains essentially an indirect-gap material even in nanocrystalline form. [84] These two cases represent distinct material classes that cannot be continuously tuned between direct and indirect character within a single platform.

The $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy system provides a rare and scientifically valuable exception. InP is a direct-gap semiconductor with both its valence-band maximum and conduction-band minimum at the Γ point (Fig. 1.3C), [93, 94] while GaP is an indirect-gap semiconductor

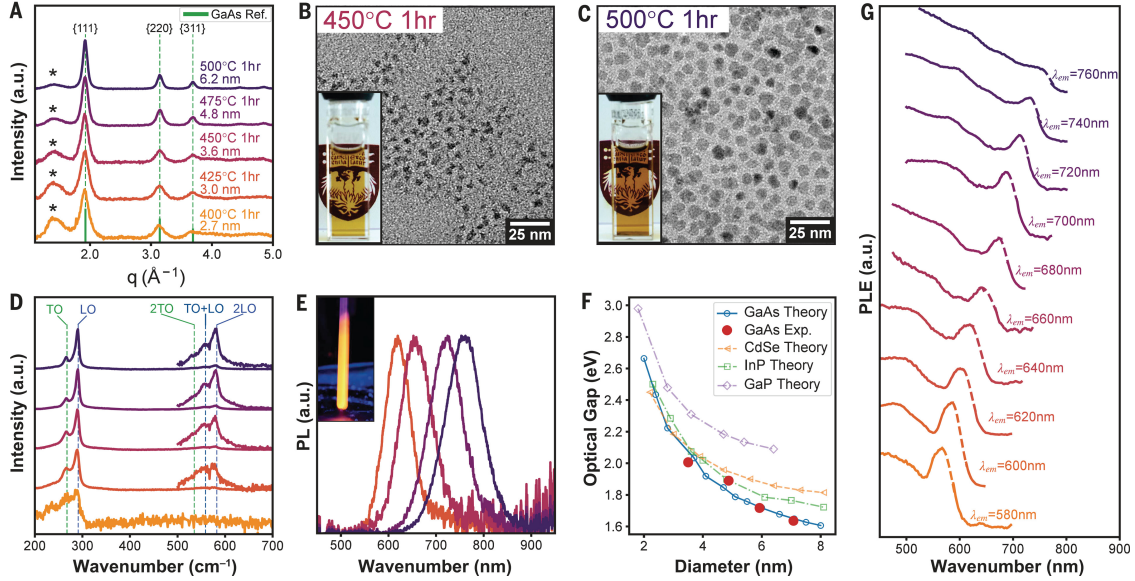


Figure 1.2: Direct synthesis of GaAs NCs in molten salt solvents. The figure is adapted from Ref. [80] (Copyright 2024 American Chemical Society). (A) Powder XRD patterns of colloidal GaAs NCs synthesized from $\text{Ga}[\text{GaI}_4]$ and AsI_3 in molten $\text{CsI}/\text{NaI}/\text{KI}$ eutectic at temperatures from 425° to 500°C. The sample synthesized at 400°C was prepared by using a KGaI_4 solvent. The peaks indicated with asterisks originate from x-ray scattering from the organic ligand shell. (B and C) TEM images of colloidal GaAs NCs synthesized at (B) 450°C and (C) 500°C. (Insets) Photos of the same samples as colloidal solutions in toluene. (D) Raman spectra of colloidal GaAs NCs with reference GaAs Raman modes indicated as dotted lines. (E) Room-temperature PL from GaAs NCs synthesized at 425° to 500°C. (Inset) Photo of GaAs NCs synthesized at 425°C under ultraviolet illumination. (F) Calculated size-dependent optical gap and PL peak position for GaAs NCs compared with those of InP, GaP, and CdSe. Exp., experiment. (G) Room-temperature PLE spectra recorded at different emission wavelengths for GaAs NCs.

with its conduction-band minimum at the X point (Fig. 1.3A). [93] These two materials form solid solutions at all compositions: increasing the gallium fraction raises the energy of the Γ -point conduction-band minimum and lowers that of the X -point minimum, producing a crossover at a bulk composition of approximately 75% gallium (Fig. 1.3B). [92] The $\text{In}_{1-x}\text{Ga}_x\text{P}$ system therefore provides a continuously tunable platform for studying the evolution from direct-gap to indirect-gap behavior. How quantum confinement modifies this composition-driven crossover, and whether strong confinement induces additional Γ - X valley mixing, remain open questions that have not been systematically addressed. Epitaxially grown Stranski-Krastanov quantum dots offer limited access to this physics because strain-driven island formation couples size and composition, and the resulting dots are typically

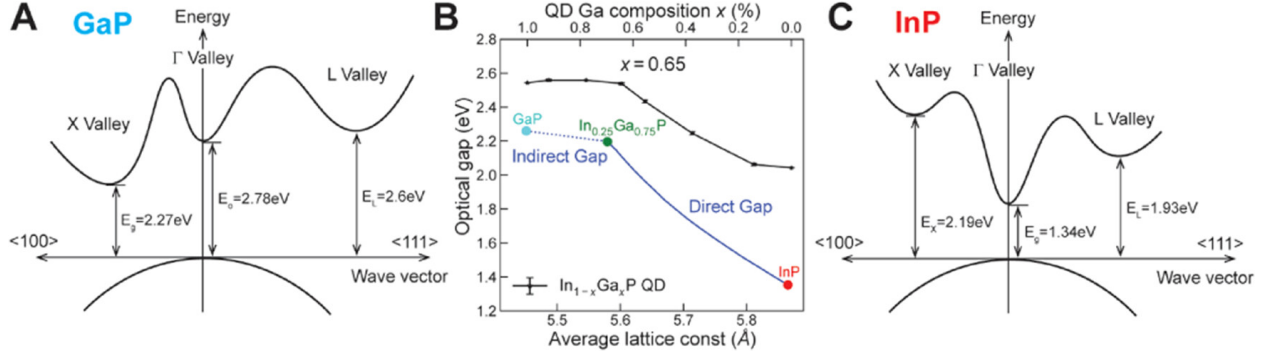


Figure 1.3: Band structures of bulk GaP (A) and InP (C). (B) Composition dependence of the band gap and lattice constant of bulk $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloys at 300 K (blue line), based on previously reported data in refs [90] and [91]. Black squares denote theoretical predictions for the composition-dependent band gap of 4 nm diameter $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals, calculated using the semi-empirical pseudopotential model described below. Panel (A) is adapted with permission from Ref. [92] (Copyright 1971 American Physical Society). Panel (C) is adapted with permission from Ref. [93] (Copyright 1986 American Physical Society).

too large for strong confinement. [95] Colloidal synthesis via molten-salt cation exchange overcomes these constraints: starting from well-characterized InP nanocrystals dispersed in a gallium-containing molten salt, high-temperature annealing drives solid-state diffusion of gallium into the lattice with coupled out-diffusion of indium, producing $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals whose composition can be controlled independently of particle size. [90, 91, 96]

From both a materials design and a theoretical perspective, these alloyed nanocrystals are compelling. Composition provides an additional control knob (beyond size and shape) for modulating band-edge energies, optical transition strengths, and carrier dynamics, a tunability that is a recurring theme throughout this dissertation. At the same time, alloyed nanocrystals present a distinct modeling challenge: the training data available for machine-learned models typically consist of calculations on ordered bulk phases at discrete compositions, yet the physical systems of interest are disordered alloys sampling a continuous compositional space. Alloyed nanocrystals therefore serve as a stringent test of model transferability, probing how well both traditional semi-empirical methods and data-driven approaches generalize to regimes not fully covered by their training sets. With experimental access to high-quality colloidal binary and alloyed III-V nanocrystals, it is now possible to move beyond simply establishing the presence of band-edge emission and toward a quantitative, microscopic understanding of their photophysics. This includes systematic analysis of how excitonic structure, radiative recombination dynamics, exciton-phonon coupling mechanisms, and band-edge character evolve with nanocrystal size, shape, and alloy composition under strong quantum confinement.

1.3 Exciton-phonon coupling and charge carrier dynamics in III-V nanocrystals

Beyond static electronic and optical properties, the dynamical behavior of photoexcited carriers provides a deeper window into the photophysics of semiconductor nanocrystals. Upon photoexcitation, high-energy (“hot”) excitons relax through interactions with phonons, and this exciton-phonon coupling (EXPC) governs nonradiative cooling rates, coherent quantum dynamics, and ultimately the efficiency of energy conversion and light emission. In bulk semiconductors, energy and quasi-momentum are transferred between charge carriers and phonons through Fröhlich-type and deformation-potential-type interactions. [97–99] Quantum confinement fundamentally alters this picture: the discretization of electronic energy levels and the relaxation of momentum selection rules create a phonon bottleneck in relaxation dynamics and give rise to coherent exciton-phonon phenomena that are absent in bulk. [100–103] Extensive research has focused on quantifying EXPC and understanding how it influences hot-exciton cooling and other relaxation channels, particularly in well-studied model systems such as CdSe quantum dots. [104–110]

Alloying introduces qualitatively new complexity into exciton dynamics that cannot be captured by models developed for binary quantum dots. In binary systems, the conventional picture describes excitons formed in a spin-allowed “bright” state that relax to a spin-forbidden “dark” state, producing red-shifted emission. [111–113] While this three-level model captures the temperature dependence of photoluminescence lifetimes in InP and CdSe quantum dots, it oversimplifies the exciton fine structure. In alloyed systems such as $\text{In}_{1-x}\text{Ga}_x\text{P}$, the reduction of crystal symmetry by compositional disorder lifts level degeneracies, producing a denser manifold of excitonic states with reduced energy spacings. [79, 114] This modified level structure changes how excitons couple to optical and acoustic phonons: direct-gap excitons couple more strongly to longitudinal optical (LO) phonon modes, while the closer energy spacing in indirect-gap compositions facilitates faster relaxation and decoherence when level spacings fall below a single phonon quantum. The interplay between exciton level structure and EXPC thus emerges as the key factor governing both the timescale of hot-exciton cooling and the identity of energy-retaining states that slow carrier relaxation.

Resolving these dynamical phenomena requires both advanced spectroscopic techniques and atomistic theoretical methods. Experimentally, EXPC can be probed through quantum coherences observed in time-resolved spectroscopy, including transient absorption and two-dimensional electronic spectroscopy (2DES), where oscillatory signals at phonon frequencies appear on femtosecond to picosecond timescales following photoexcitation. [104, 115–121] Complementarily, resonance Raman spectroscopy provides a steady-state measure of coupling strengths to specific phonon modes. [122, 123] On the theoretical side, atomistic semi-empirical pseudopotential methods, combined with the Bethe-Salpeter equation for excitonic effects and polaron-transformed Redfield theory for open-quantum-system dynamics, provide access to excitonic state-specific EXPC and relaxation rates that are beyond the reach of continuum effective-mass models. [124–128] This joint experimental-theoretical

approach, applied in this dissertation to alloyed III-V quantum dots, reveals that composition tunes not only band gaps but also the intricate nonradiative relaxation pathways and coherent dynamics that determine the photophysical performance of quantum dot materials.

In this dissertation, we develop and apply machine-learning-enabled atomistic simulation frameworks for predicting the electronic, optical, and dynamical properties of semiconductor nanomaterials. By combining semi-empirical pseudopotential theory with data-driven learning, we establish a unified computational approach capable of capturing complex photophysical phenomena, from single-particle electronic structure and excitonic fine structure to exciton-phonon coupling and ultrafast carrier dynamics, all at system sizes and compositional complexities relevant to experiment.

The remainder of this dissertation is organized as follows. Chapter 2 introduces the theoretical and computational foundations of this work. We present the atomistic semi-empirical pseudopotential framework, describe the machine-learning architecture of DeepPseudopot, a neural-network model of local screened pseudopotentials trained on DFT and GW-level bulk band structures. We discuss key design choices including the treatment of non-local and spin-orbit coupling terms. This chapter also covers the construction of high-quality training datasets and the development of the associated open-source software. Chapter 3 applies the framework to colloidal III-V semiconductors and their alloys, a class of materials that has gained renewed relevance in the nanocrystal regime following advances in molten-salt synthesis. We examine the electronic and optical properties of GaAs nanocrystals and alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ quantum dots, connecting computed excitonic observables to experimental measurements, including optical gaps, radiative lifetimes, and absorption spectra. This chapter also presents an atomistic linear-response description of phonon-resolved single-nanocrystal emission, linking exciton-phonon coupling to experimentally observed spectral lineshapes in GaAs nanocrystals. Chapter 4 moves beyond static electronic structure to investigate coupled electronic-nuclear dynamics in alloyed III-V quantum dots. Combining atomistic pseudopotential calculations with polaron-transformed Redfield theory and two-dimensional electronic spectroscopy measurements, we elucidate how alloy composition reshapes ultrafast hot-exciton relaxation pathways, exciton-phonon coupling across the excitonic manifold, and electronic coherences. Finally, Chapter 5 summarizes the key contributions and discusses future directions.

Chapter 2

DeepPseudopot, a machine-learned semi-empirical pseudopotential architecture for nanomaterials

This chapter includes material adapted from: Kailai Lin, Matthew J. Coley-O'Rourke, and Eran Rabani. **“Deep-learning atomistic semi-empirical pseudopotential model for nanomaterials,”** *npj Computational Materials* 11, 381 (2025). [129] This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 International License.

A broad hierarchy of electronic structure methods has been developed to describe materials across different physical regimes and system sizes. These approaches span from effective model Hamiltonians, such as tight-binding and Hubbard models, [130, 131] to first-principles methods based on density functional theory (DFT), [132] to many-body perturbation theory techniques including the GW approximation and the Bethe–Salpeter equation (BSE), [57, 133–135] and ultimately to non-perturbative frameworks designed for strongly correlated systems. [136, 137] Each level in this hierarchy reflects a trade-off between physical accuracy, computational cost, and the accessible length and time scales of simulation.

First-principles methods such as density functional theory (DFT) are widely used to study the electronic structure of materials. [3, 138] However, due to the limitations of approximate exchange-correlation functionals, DFT often underestimates band gaps and yields inaccurate excitation energies compared to experimental measurements. [139] Several approaches have been used to partially correct these deficiencies at the mean-field level, including hybrid exchange-correlation functionals, the modified Becke-Johnson mBJ functional, [140] and the DFT + U method. [141, 142] To address these limitations more systematically, state-of-the-art approaches employ many-body perturbation theory (MBPT) within the GW approximation, which more accurately accounts for electron-electron interactions via the expansion of the self-energy and provides improved predictions of quasiparticle energies and excited states. [57, 143–145] Spin-orbit coupling can be incorporated into this approach, and optical

absorption spectra can be obtained by solving the Bethe-Salpeter Equation (BSE) on top of GW. [135, 146] Despite their improved accuracy, these first-principles methods incur a high computational cost, rendering them impractical for routine simulations of large NCs in the moderate to weak confinement regimes. [147] In particular, GW/BSE calculations have at least quartic scaling with system size, further compounding this challenge.

Semi-empirical electronic structure methods provide an alternative modeling strategy that seeks to balance computational efficiency with physical fidelity. Approaches such as pseudopotential methods, [148–150] tight-binding models, [151, 152] and Wannier-function-based tight-binding Hamiltonians [153, 154] employ parametrized effective Hamiltonians to simplify the electronic structure problem. The parameters in these models are typically fitted to experimental measurements or high-level first-principles reference data, such as GW/BSE calculations, enabling simulations of large nanocrystal systems with a favorable balance between computational cost and accuracy. [155]

While successful, these approaches are ultimately limited by the expressiveness of their chosen functional forms and by restricted parameterization strategies, which constrain transferability across diverse chemical environments. This limitation becomes increasingly severe in nanomaterials, where strong confinement, surface effects, and compositional heterogeneity cast physical significant impact on the resulting electronic structure. Machine learning provides a natural extension of the semi-empirical methods by replacing low-dimensional, manually designed parameterizations with high-dimensional, flexible representations learned directly from accurate reference data. Meanwhile, the ML models can be constructed to retain the physically motivated structure of effective Hamiltonian models. By combining the physics basis and interpretability of semi-empirical pseudopotential theory with the expressive power of data-driven learning, machine learning enables a systematic generalization of classical pseudopotential approaches.

In this chapter, we introduce DeepPseudopot, a machine-learned semi-empirical pseudopotential architecture designed for accurate and scalable simulations of nanomaterial electronic properties. Section 2.1 reviews the foundations of traditional pseudopotential theory, analyzing its strengths and limitations and motivating the development of an ML-augmented formulation. Section 2.2 presents the architectural design of DeepPseudopot, including the decomposition of the Hamiltonian into local, nonlocal, and spin-orbit coupling components within a spinor plane-wave basis. Section 2.3 describes the preparation of high-quality ab initio reference data, including bulk band structures, deformation potentials, and electron–phonon couplings, and discusses how these data are incorporated into the training procedure. Section 2.4 introduces the open-source software package developed in conjunction with the model and discusses the role of software engineering principles in ensuring reproducibility, extensibility, and long-term sustainability. Sections 2.5 and 2.6 present benchmark results and applications of the DeepPseudopot model to silicon allotropes and a representative family of III–V semiconductors, respectively. Finally, Section 2.7 extends the framework using atomic environment descriptors beyond periodic boundary conditions, enabling applications to finite systems such as isolated molecules and, ultimately, ligand pseudopotentials.

2.1 Traditional pseudopotential theory

Solving the many-electron Schrodinger equation has long been a central challenge in quantum chemistry and condensed matter physics. The explicit treatment of electron–electron interactions in realistic materials systems rapidly becomes computationally intractable as system size increases. Consequently, many practical electronic structure approaches adopt an effective single-particle picture, in which the complex many-body interactions are incorporated into an effective potential acting on individual electrons. Within this framework, the electronic Hamiltonian takes the generic form:

$$H = -\frac{1}{2}\nabla^2 + V(\mathbf{r}), \quad (2.1)$$

where $V(\mathbf{r})$ represents an effective one-electron potential.

Pseudopotential theory is a particular realization of this idea that arises from a key observation: core electrons are typically chemically inert and primarily influence valence electrons through their screening of the nuclear potential.

Under this assumption, the strong ionic core potential and tightly bound core states are not treated explicitly. Instead, their net effect is incorporated into a smoother effective potential acting on valence electrons alone. This results in valence pseudo-wavefunctions that are smooth (or substantially smoother than the real wavefunctions) in the core region. This smoothness is crucial in practice because it dramatically improves basis set convergence, especially in plane-wave expansions, and enables efficient simulations of large systems.

One can view the pseudopotential as an operator that reproduces the valence eigenvalues while projecting out the explicitly treated core subspace.

$$V_p(\mathbf{r}) = V(\mathbf{r}) + \sum_t (E_{\mathbf{k}} - E_t) |\phi_t\rangle \langle \phi_t|, \quad (2.2)$$

where $V_p(\mathbf{r})$ is the pseudopotential, $V(\mathbf{r})$ is the true ionic potential, and $|\phi_t\rangle$ is a core eigenstate with eigenvalue E_t . The projection term cancels the real potential within the core region and enforces orthogonality to the core states, producing smooth valence pseudo-eigenstates and a soft effective potential.

This construction is also where non-locality of the pseudopotential generally enters. Because the core states have explicit angular momentum, the projection will depend on the orbital channel. In practice, this angular momentum dependence is expressed through a separable nonlocal projector that depends on the angular momentum quantum number, and has been shown to improve transferability across materials and bonding environments. [148, 156]

Early work by Cohen and co-workers established pseudopotentials as a practical and physically motivated tool for calculating the electronic structure of crystalline solids, particularly semiconductors with diamond and zinc-blende crystal structures. [157] By exploiting the separation between chemically inert core states and chemically active valence states, pseudopotential methods significantly simplify electronic structure calculations while preserving

key band structure properties. Subsequent developments introduced nonlocal pseudopotentials, [148] further improving transferability across different chemical environments and bonding configurations. [149] The reduced computational cost and retained fidelity in describing band structure, optical response functions and electronic charge densities make the pseudopotential family of methods particularly suited for understanding defects, surfaces, interfaces, etc. for a wide range of semiconductor materials.

In practice, the computational efficiency of pseudopotential methods is closely tied to their natural expression in a plane-wave basis. In reciprocal space, the pseudopotential is expressed as a sum over atomic contributions multiplied with crystal structure factors. For a system containing N_{at} atoms, the total pseudopotential can be written as

$$V(\mathbf{G}) = \sum_{\alpha}^{N_{\text{at}}} S_{\alpha}(\mathbf{G}) V_{\alpha}(\mathbf{G}), \quad (2.3)$$

where $V_{\alpha}(\mathbf{G})$ denotes the atomic pseudopotential associated with atom α , and the structure factor is given by

$$S_{\alpha}(\mathbf{G}) = e^{i\mathbf{G} \cdot \mathbf{R}_{\alpha}}. \quad (2.4)$$

In bulk crystalline systems, the reciprocal-space pseudopotential $V(\mathbf{G})$ need only be defined at reciprocal lattice vectors $\mathbf{G}$ that satisfy the Bragg condition. However, when translational symmetry is broken, as in finite systems or nanostructures, this constraint no longer applies. To extend pseudopotential methods to such systems, the reciprocal-space potential must be defined as a continuous function of $\mathbf{G}$. In practice, this is achieved by choosing a suitable functional form for $V(\mathbf{G})$ and fitting it to reproduce bulk band structures. This continuous representation can then be Fourier transformed to obtain a real-space pseudopotential, enabling straightforward adaptation to nanostructures with reduced or broken translational symmetry.

To better describe the structural and electronic complexity of realistic nanocrystal systems, semi-empirical pseudopotential models were introduced and further developed during the 1970s and 1980s. Semi-empirical pseudopotential methods generalize first-principles pseudopotentials by fitting model parameters to experimental data or to high-level electronic structure calculations, rather than deriving them entirely from first principles. While this introduces an element of empiricism, it allows the resulting models to accurately reproduce essential electronic properties at greatly reduced computational cost.

A particularly influential class of such approaches is the local-density-derived semi-empirical pseudopotential method (SEPM), developed and applied extensively by Wang, Lin, and co-workers. [150] In this framework, pseudopotentials are constructed by inverting the self-consistent screened local density approximation (LDA) potentials of bulk materials, followed by adjustments to reproduce experimental excitation energies. By performing calculations over an ensemble of bulk crystal structures and averaging the resulting screened LDA potentials, a transferable, structurally averaged, and approximately spherically symmetric pseudopotential can be obtained. Despite this averaging and empirical adjustments, the resulting pseudopotentials retain high fidelity to the underlying LDA eigenstates. The SEPM

and its variants have been successfully applied to a wide range of semiconductor nanocrystal systems, providing insight into their electronic structure, photophysics, spectroscopy, and charge carrier dynamics. In these methods, simple functional forms are used to interpolate the reciprocal-space pseudopotential across different form factors, which are then numerically Fourier transformed to obtain real-space potentials suitable for nanostructures with broken translational symmetry. [155, 158, 159]

Subsequent extensions by Rabani and collaborators incorporated additional physical effects into the pseudopotential framework, including spin-orbit coupling, strain, deformation potentials, and electron-phonon coupling terms. [108, 128, 160, 161] These developments further enhanced the descriptive power of semi-empirical pseudopotential methods, enabling the study of excited-state properties and dynamical processes in nanomaterials within a computationally efficient Hamiltonian framework.

Overall, traditional semi-empirical pseudopotential methods exhibit several notable strengths. They offer high computational efficiency, retain clear physical interpretability through an effective Hamiltonian formulation, and are well suited for simulations of large nanostructures that are inaccessible to fully *ab initio* approaches. The semi-empirical nature also enables adjustments of energy-related observables (such as gap and excitation energies) to correct for systematic deviations of *ab initio* results to experimental measurements. In the meantime, these methods also suffer from inherent limitations. The reliance on manual parametrization restricts transferability across diverse chemical environments, while the use of low-dimensional functional forms complicates the incorporation of nonlocal, relativistic, and environment-dependent effects. Moreover, traditional semi-empirical approaches lack a systematic pathway for controlled improvement, motivating the development of more flexible and extensible modeling strategies.

2.2 DeepPseudopot: model design and implications

Traditional semi-empirical pseudopotential methods provided an efficient and physically transparent framework for modeling the electronic structure of bulk semiconductors and nanostructures. Their success relies on reducing the many-electron problem to an effective single-particle Hamiltonian, while capturing essential band structure properties through carefully constructed local, non-local, and relativistic pseudopotential terms that reproduce bulk material properties. However, the reliance on fixed functional forms of the local, non-local and spin-orbit coupling pseudopotentials and the manual parametrization limits their transferability and hinders systematic improvement, particularly when targeting complex materials or properties beyond those included in the original fitting procedure.

Machine learning offers a natural route to generalize semi-empirical pseudopotential theory by replacing the low-dimensional analytic parametrizations with flexible, data-driven representations, while retaining the underlying Hamiltonian structure and physical interpretability. In this section, we introduce the use of machine learning techniques in parametrizing semi-empirical pseudopotentials, demonstrating more scalable and accurate simulations of

the electronic, optical, and dynamical properties of nanomaterials. Building on the physical foundations of pseudopotential theory, we develop a transferable deep-learning atomistic pseudopotential surrogate model, termed *DeepPseudopot*, which combines a neural-network representation of the local screened pseudopotential with analytic non-local and spin-orbit coupling corrections.

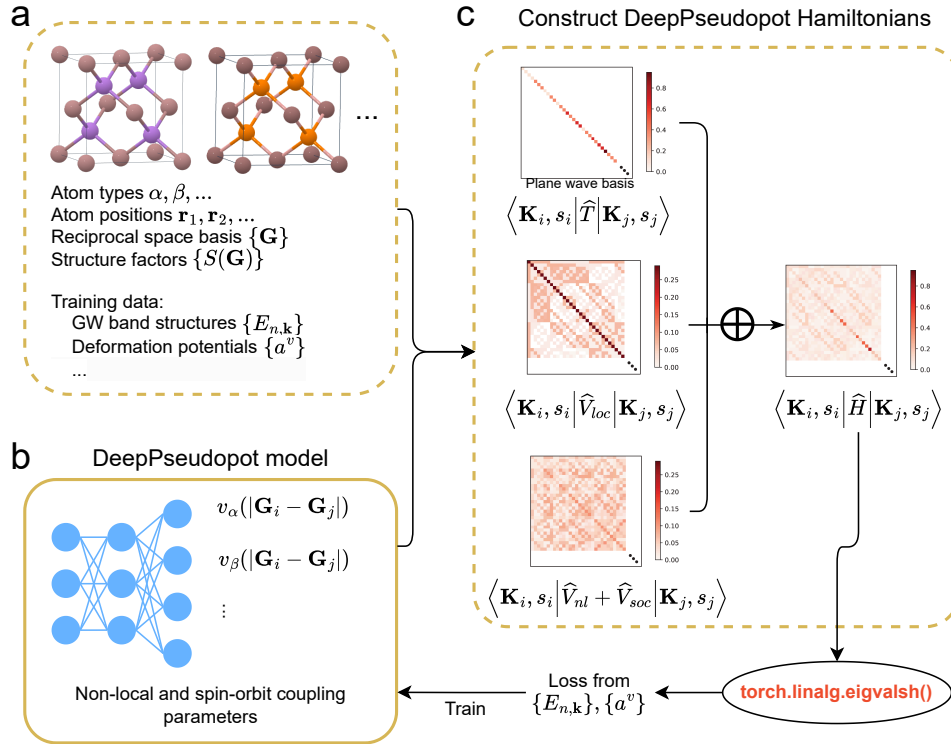


Figure 2.1: Workflow for developing the DeepPseudopot model. (a) Reference data generation. Quasiparticle band structures and hydrostatic deformation potentials are computed using DFT+GW for multiple crystal structures. (b) Model setup. The atomistic machine learning model is initialized, with the local pseudopotential represented by a neural network and the non-local and spin-orbit coupling terms modeled by parameterized functional forms. (c) Hamiltonian construction and model training. The DeepPseudopot Hamiltonian is constructed from structure factors, wavevector data, and the model pseudopotentials, then diagonalized to obtain the predicted quasiparticle band structures and deformation potentials. The model is trained by minimizing the loss function based on these properties.

The machine learning semi-empirical pseudopotential model employs a non-local single-electron Hamiltonian to compute the quasiparticle band structures and deformation poten-

tials in a plane wave spinor basis, as well as the electronic structure of nanoscale systems using a real-space grid basis. The Hamiltonian is given by

$$\hat{H} = \hat{T} + \hat{V}_{\text{loc}} + \hat{V}_{\text{nl}} + \hat{V}_{\text{soc}}, \quad (2.5)$$

where $\hat{V}_{\text{loc}}$ is the local pseudopotential that acts equally on all angular momentum channels, $\hat{V}_{\text{nl}}$ is an angular momentum-dependent correction to the local pseudopotential, and $\hat{V}_{\text{soc}}$ is the spin-orbit dependent pseudopotential. The pseudopotential terms are given as a sum over atom-centered potentials within the simulation cell, which corresponds to a single unit cell for bulk systems or the full nanocrystal for finite systems.

$$\hat{V}_{\text{loc}} = \sum_{\alpha}^{\text{Nat}} \hat{v}_{\text{loc}}^{\alpha}, \quad \hat{V}_{\text{nl}} = \sum_{\alpha}^{\text{Nat}} \hat{v}_{\text{nl}}^{\alpha}, \quad \hat{V}_{\text{soc}} = \sum_{\alpha}^{\text{Nat}} \hat{v}_{\text{soc}}^{\alpha}. \quad (2.6)$$

This approach generates the effective potential of a given geometry configuration in a single pass, bypassing the need for computationally intensive self-consistent field (SCF) iterations.

The local pseudopotential is modeled using a multi-layer fully connected neural network (as illustrated in Fig. 2.1 and Eq. (2.7)), [162] taking as input the reciprocal space distance $G = |\mathbf{G}_i - \mathbf{G}_j|$, where $\mathbf{G}$ denotes the reciprocal space basis. The output tensor size is equal to the number of atom types in the system(s). To enforce the decay of the local pseudopotential in reciprocal space and improve convergence with respect to the kinetic energy cutoff, the activation function in the final layer is replaced with a Gaussian function. The local pseudopotential is given by:

$$v_{\text{loc}}^{\alpha}(G) = \left[(h^H \circ \dots \circ h^2 \circ h^1)(G) \right]_{\alpha}, \quad (2.7)$$

where $h^i(x) = \sigma(W^i x + b^i)$ is the output of the i -th hidden layer, σ is an activation function, and W^i and b^i are the weights and bias tensors. [162] In the plane wave spinor basis $|\mathbf{K}, s\rangle$, the local pseudopotential Hamiltonian matrix elements at wavevector $\mathbf{k}$ are expressed as:

$$\begin{aligned} \langle \mathbf{K}_i, s_i | \hat{v}_{\text{loc}}^{\alpha} | \mathbf{K}_j, s_j \rangle = \\ \frac{1}{\Omega} e^{i(\mathbf{G}_i - \mathbf{G}_j) \cdot \mathbf{R}_{\alpha}} v_{\text{loc}}^{\alpha}(|\mathbf{G}_i - \mathbf{G}_j|) \delta_{s_i, s_j}, \end{aligned} \quad (2.8)$$

where $\mathbf{K} = \mathbf{k} + \mathbf{G}$ for all $\mathbf{G}$ of the reciprocal space basis, $e^{i(\mathbf{G}_i - \mathbf{G}_j) \cdot \mathbf{R}_{\alpha}}$ is the structure factor $S^{\alpha}(G)$ for atom α , and Ω is the unit cell volume. We assume spherical symmetry of the local pseudopotential around each atom, which simplifies and accelerates the inverse Fourier transform to real space. The atomic potential does not explicitly encode neighbor information, and is shown to be sufficient for the systems studied here. Environment-dependent descriptors can be systematically incorporated into the model to address more complex systems, as discussed in Section III. The resulting continuous local potential can be used to construct the nanocrystal potential in the grid basis. Asymmetry in the total electronic potential is captured by the non-local and spin-orbit coupling terms.

The non-local and SOC pseudopotentials correct the local term, capturing angular-momentum-dependent and relativistic effects. In our model, both terms are assumed to act only on the $l = 1$ angular momentum channel (we assume $l = 0$ is the local channel) and are represented using simple analytic forms inspired by earlier work. [148, 150, 161, 163]

$$\hat{v}_{\text{nl}}^\alpha = \left[\theta_{\text{nl}1}^\alpha e^{-r^2} + \theta_{\text{nl}2}^\alpha e^{-(r-\rho)^2} \right] \hat{P}_{l=1}^\alpha, \quad (2.9)$$

$$\hat{v}_{\text{soc}}^\alpha = \left[\theta_{\text{soc}}^\alpha e^{-\frac{r^2}{w^2}} \right] \hat{\mathbf{L}}^\alpha \cdot \hat{\mathbf{S}} \hat{P}_{l=1}^\alpha, \quad (2.10)$$

where $\hat{P}_{l=1}^\alpha$ is the projector onto the $l = 1$ orbitals of atom type α , $\hat{\mathbf{L}}^\alpha$ is the orbital angular momentum operator, $\hat{\mathbf{S}}$ is the spin operator, and $\theta_{\text{nl}1}^\alpha, \theta_{\text{nl}2}^\alpha, \theta_{\text{soc}}^\alpha$ are the non-local and SOC parameters. We choose to use simple piece-wise Gaussian functions with adjustable prefactors instead of neural networks due to the otherwise prohibitively high computational cost of evaluating and converging the matrix elements in the plane wave spinor basis, given by Eq. (2.11). To further reduce computational overhead, the parameters ρ and w were fixed to 1.5 and 0.7 Bohr, respectively. As shown in this work, these approximations—when coupled with the flexibility of the neural network representation of the local pseudopotential—are sufficient to achieve high-quality fits to bulk band structure properties.

In the plane wave spinor basis, the matrix elements of the non-local and SOC pseudopotentials are expressed as

$$\begin{aligned} \langle \mathbf{K}_i, s_i | \hat{v}_{\text{nl}}^\alpha | \mathbf{K}_j, s_j \rangle &= \frac{12\pi}{\Omega} \frac{\mathbf{K}_i \cdot \mathbf{K}_j}{K_i K_j} e^{i(\mathbf{G}_i - \mathbf{G}_j) \cdot \mathbf{R}_\alpha} I_{\text{nl}}, \\ \langle \mathbf{K}_i, s_i | \hat{v}_{\text{soc}}^\alpha | \mathbf{K}_j, s_j \rangle &= -i \frac{12\pi}{\Omega} \frac{\mathbf{K}_i \times \mathbf{K}_j}{K_i K_j} e^{i(\mathbf{G}_i - \mathbf{G}_j) \cdot \mathbf{R}_\alpha} I_{\text{soc}} \cdot \mathbf{S}_{s_i, s_j}, \end{aligned} \quad (2.11)$$

where the integrals are defined as $I_{\text{nl}} = \int_0^\infty dr r^2 j_1(K_i r) \left(a_{\text{nl}1}^\alpha e^{-r^2} + a_{\text{nl}2}^\alpha e^{-(r-\rho)^2} \right) j_1(K_j r)$, $I_{\text{soc}} = \int_0^\infty dr r^2 j_1(K_i r) \left(a_{\text{soc}}^\alpha e^{-\frac{r^2}{w^2}} \right) j_1(K_j r)$, $j_1(K_j r)$ is the spherical Bessel function of order 1, and $\mathbf{S}_{s_i, s_j}$ are matrix elements of the spin operator.

2.3 Model training on band structures and electron-phonon coupling

Highly accurate reference data from DFT+GW calculations were prepared to train the DeepPseudopot parameters, including the neural network weights and biases for the local pseudopotentials as well as the non-local and SOC parameters. Specifically, we generated band structure data along a densely sampled high-symmetry path in the Brillouin zone and extracted hydrostatic volume deformation potentials. The band structure data trains the pseudopotential model to capture electronic eigenenergies and their dispersion, while

the deformation potentials quantify how the eigenenergies respond to local lattice strains, which is crucial for accurately modeling perturbative electron-phonon coupling. The MBPT correction within GW approximation is essential in this workflow, as it addresses the self-interaction error in standard density functional approximations. Compared to conventional DFT, GW provides significantly more accurate quasiparticle band gaps and excited-state properties, yielding better agreement with experimental measurements in semiconducting materials.

Hydrostatic volume deformation potentials describe the change and sensitivity of inter-band transition energies under isotropic strain:

$$a_t^V = \frac{dE_t}{d \ln V}, \quad (2.12)$$

where E_t is the transition energy and V is the (deformed) cell volume. To avoid complications associated with the ambiguous absolute energy reference in periodic systems, [164, 165] we only calculated deformation potentials for interband transitions. These quantities were evaluated using a finite difference approach by uniformly expanding and contracting the unit cell and extracting the deformation potential from the slope of the transition energy. This workflow of data preparation from high-level theory can be easily extended to other bulk properties, including electron-phonon coupling tensors, dielectric constants, and charge densities.

Although the band energies and their strain response provide important constraints on the pseudopotential, they do not by themselves guarantee an accurate description of the coupling between electronic states and nuclear motion, particularly in polar materials where long-range Fröhlich-type interactions become important beyond the local deformation-potential limit. [98, 166] Such electron-phonon couplings are nevertheless essential for modeling non-adiabatic vibronic interactions and the resulting charge-carrier dynamics in nanosystems. In particular, they govern processes such as phonon-assisted relaxation, hot-carrier cooling, and decoherence, as discussed further in Chapter 4. To enable accurate parameterization for these applications, DeepPseudopot must therefore be trained not only to reproduce quasiparticle energies and deformation potentials, but also to recover accurate bulk electron-phonon coupling (EPC) matrix elements. We computed *ab initio* EPC using density functional perturbation theory (DFPT) [167, 168] in Quantum Espresso [169] and, in non-periodic cases, using the `eph` module in PySCF. [170] These calculations provide the reference coupling matrix elements needed to train the model to more faithfully capture the derivatives of the Hamiltonian that govern lattice-driven electronic dynamics.

The overall training workflow for the DeepPseudopot model is also illustrated in Fig. 2.1. During training, we iterated over the wavevectors $\mathbf{k}$ and constructed the DeepPseudopot Hamiltonian, including the kinetic energy, local pseudopotential, non-local and spin-orbit coupling terms, in a converged plane wave spinor basis. We computed the eigenvalues of the resulting Hamiltonian using the complex Hermitian eigenvalue solver (`torch.linalg.eigvalsh()`) from PyTorch, which allows for efficient backpropagation through the operation. Degenerate

eigenvalues were distinguished by maximizing the overlap of eigenvectors between adjacent $\mathbf{k}$ -points, following a Wannier-like process. [171] For efficiency, the training was first carried out on a sparsely sampled $\mathbf{k}$ -point grid chosen to retain all high-symmetry points together with the relevant band edges. This strategy substantially reduces the computational cost while remaining accurate in practice, because a smooth pseudopotential typically produces smoothly varying band dispersions.

The deformation potentials were evaluated for selected interband transitions using the same finite-difference procedure described above. In addition to these transition-level responses, we also trained DeepPseudopot against bulk electron-phonon coupling (EPC) matrix elements obtained from first-principles calculations. For a phonon perturbation associated with atom A and Cartesian direction α , the EPC matrix element between Bloch states $\psi_{n\mathbf{k}}$ and $\psi_{m,\mathbf{k}+\mathbf{q}}$ is defined as

$$g_{nm\mathbf{k}\mathbf{q}}^{A\alpha} = \left\langle \psi_{n\mathbf{k}} \left| \frac{\partial \hat{V}_{\text{loc}}}{\partial R_{A\alpha}} \right| \psi_{m,\mathbf{k}+\mathbf{q}} \right\rangle, \quad (2.13)$$

where n and m label the electronic bands, $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$ are crystal momenta, $\mathbf{q}$ is the phonon wavevector, and $R_{A\alpha}$ denotes the α -component of the position of atom A . In the present implementation, we focus on the derivative of the local pseudopotential, which provides the dominant contribution needed to assess and train the lattice-driven couplings in the bulk model.

Expanding the Bloch eigenstates in the plane-wave spinor basis,

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad (2.14)$$

the coupling matrix element becomes

$$g_{nm\mathbf{k}\mathbf{q}}^{A\alpha} = \sum_{\mathbf{G}, \mathbf{G}'} c_{n\mathbf{k}}^*(\mathbf{G}) c_{m,\mathbf{k}+\mathbf{q}}(\mathbf{G}') \left\langle \mathbf{k} + \mathbf{G} \left| \frac{\partial \hat{V}_{\text{loc}}}{\partial R_{A\alpha}} \right| \mathbf{k} + \mathbf{q} + \mathbf{G}' \right\rangle. \quad (2.15)$$

The derivative in the plane-wave basis can be derived as follows.

$$\left\langle \mathbf{G} \left| \frac{\partial \hat{V}_{\text{loc}}}{\partial \tau_{\alpha}} \right| \mathbf{G}' + \mathbf{q} \right\rangle = \frac{1}{\Omega} \int_{\text{cell}} d^3\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\partial \sum_{\alpha, \mathbf{R}} v_{\alpha}(\mathbf{R} + \mathbf{r} - \tau_{\alpha})}{\partial \tau_{\alpha}} \quad (2.16)$$

$$= \frac{1}{\Omega} \int_{\text{cell}} d^3\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\alpha, \mathbf{R}} \frac{\partial v_{\alpha}(\mathbf{R} + \mathbf{r} - \tau_{\alpha})}{\partial (\mathbf{R} + \mathbf{r} - \tau_{\alpha})} \frac{\partial (\mathbf{R} + \mathbf{r} - \tau_{\alpha})}{\partial \tau_{\alpha}} \quad (2.17)$$

$$= -\frac{1}{\Omega} \int_{\text{cell}} d^3\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \nabla_{\mathbf{r}} \sum_{\alpha, \mathbf{R}} v_{\alpha}(\mathbf{R} + \mathbf{r} - \tau_{\alpha}) \quad (2.18)$$

where Ω is the unit cell volume. $\mathbf{k} = \mathbf{G} - \mathbf{G}' - \mathbf{q}$. $\mathbf{R}$ indicate the sum over all unit cells. $\mathbf{R}_\alpha$ is the position. We then integrate by parts:

$$\int_{cell} d^3\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \nabla_{\mathbf{r}} f(\mathbf{r}) = \int_{cell} d^3\mathbf{r} \nabla_{\mathbf{r}} [e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r})] - \int_{cell} d^3\mathbf{r} \nabla_{\mathbf{r}} [e^{i\mathbf{k}\cdot\mathbf{r}}] f(\mathbf{r}) \quad (2.19)$$

Since $f(\mathbf{r})$ is periodic over the unit cell, the first term equals zero. Therefore,

$$\left\langle \mathbf{G} \left| \frac{\partial \hat{V}_{loc}}{\partial \tau_\alpha} \right| \mathbf{G}' + \mathbf{q} \right\rangle = \frac{1}{\Omega} \int_{cell} d^3\mathbf{r} \nabla_{\mathbf{r}} [e^{i\mathbf{k}\cdot\mathbf{r}}] \sum_{\alpha, \mathbf{R}} v_\alpha(\mathbf{R} + \mathbf{r} - \tau_\alpha) \quad (2.20)$$

$$= \frac{1}{\Omega} \int_{cell} d^3\mathbf{r} [i\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}}] \sum_{\alpha, \mathbf{R}} v_\alpha(\mathbf{R} + \mathbf{r} - \tau_\alpha) \quad (2.21)$$

We lastly do a change of variables $\mathbf{r}' = \mathbf{r} - \tau_\alpha$ to convert into the Fourier space of the potentials, where v_α is the real space potential around atom α , and $\tilde{v}_\alpha$ is the Fourier transform of that potential.

$$\left\langle \mathbf{G} \left| \frac{\partial \hat{V}_{loc}}{\partial \tau_\alpha} \right| \mathbf{G}' + \mathbf{q} \right\rangle = \frac{1}{\Omega} \int_{cell} d^3\mathbf{r}' [i\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}'} e^{i\mathbf{k}\cdot\tau_\alpha}] \sum_{\mathbf{R}} v_\alpha(\mathbf{R} + \mathbf{r}') \quad (2.22)$$

$$= \frac{1}{\Omega} i\mathbf{k} e^{i\mathbf{k}\cdot\tau_\alpha} \int_{cell} d^3\mathbf{r}' e^{i\mathbf{k}\cdot\mathbf{r}'} \sum_{\mathbf{R}} v_\alpha(\mathbf{R} + \mathbf{r}') \quad (2.23)$$

$$= \frac{1}{\Omega} i\mathbf{k} e^{i\mathbf{k}\cdot\tau_\alpha} \int_{\mathbf{R}^3} d^3\mathbf{r}' e^{i\mathbf{k}\cdot\mathbf{r}'} v_\alpha(\mathbf{r}') \quad (2.24)$$

$$\equiv \frac{1}{\Omega} i\mathbf{k} e^{i\mathbf{k}\cdot\tau_\alpha} \tilde{v}_\alpha(\mathbf{k}) \quad (2.25)$$

Thus, we have used the shown equality to calculate the PBC epc elements and avoid taking derivative of the pseudopotential in any manner.

$$\left\langle \mathbf{G} \left| \frac{\partial \hat{V}_{loc}}{\partial \tau_\alpha} \right| \mathbf{G}' + \mathbf{q} \right\rangle = \frac{1}{\Omega} i(\mathbf{G} - \mathbf{G}' - \mathbf{q}) e^{i(\mathbf{G} - \mathbf{G}' - \mathbf{q})\cdot\tau_\alpha} \tilde{v}_\alpha(\mathbf{G} - \mathbf{G}' - \mathbf{q}) \quad (2.26)$$

A subtle but important issue arises when these couplings are used as training targets. The matrix element $g_{nm\mathbf{k}\mathbf{q}}^{A\alpha}$ is generally complex and depends on the arbitrary phases chosen for the eigenvectors during diagonalization. Under independent phase rotations of the Bloch states,

$$\psi_{n\mathbf{k}} \rightarrow e^{i\theta_{n\mathbf{k}}} \psi_{n\mathbf{k}}, \quad \psi_{m,\mathbf{k}+\mathbf{q}} \rightarrow e^{i\theta_{m,\mathbf{k}+\mathbf{q}}} \psi_{m,\mathbf{k}+\mathbf{q}}, \quad (2.27)$$

the coupling transforms as

$$g_{nm\mathbf{k}\mathbf{q}}^{A\alpha} \rightarrow e^{-i\theta_{n\mathbf{k}}} e^{i\theta_{m,\mathbf{k}+\mathbf{q}}} g_{nm\mathbf{k}\mathbf{q}}^{A\alpha}. \quad (2.28)$$

Therefore, the complex value of an individual matrix element is not itself a gauge-invariant target.

The situation is even more delicate in degenerate subspaces. Suppose the left and right states ($\psi_{n\mathbf{k}}$ and $\psi_{m,\mathbf{k}+\mathbf{q}}$) belong to degenerate manifolds of dimensions d_n and d_m , respectively. Any unitary rotations within these manifolds produce an equally valid choice of eigenbasis. If the couplings within the two manifolds are collected into a matrix $\mathbf{g}$, then under such rotations

$$\mathbf{g} \rightarrow \mathbf{g}' = \mathbf{U}^\dagger \mathbf{g} \mathbf{W}, \quad (2.29)$$

where $\mathbf{U}$ and $\mathbf{W}$ are unitary matrices acting within the degenerate subspaces. As a result, the individual matrix elements $g_{nm\mathbf{k}\mathbf{q}}^{A\alpha}$ are not uniquely defined inside a degenerate manifold, even though the subspace as a whole is physically well defined. This ambiguity is a common issue when training machine-learning models against eigenvector-based quantities in electronic structure theory.

To remove the dependence on both arbitrary phases and degenerate-subspace gauge, we use a basis-invariant regression target constructed from the Frobenius norm of the coupling matrix,

$$\|\mathbf{g}\|_F^2 = \sum_{n=1}^{d_n} \sum_{m=1}^{d_m} |g_{nm\mathbf{k}\mathbf{q}}^{A\alpha}|^2 = \text{Tr}(\mathbf{g}^\dagger \mathbf{g}). \quad (2.30)$$

This quantity is invariant under unitary rotations within the degenerate subspaces because

$$\text{Tr}(\mathbf{g}'^\dagger \mathbf{g}') = \text{Tr}(\mathbf{W}^\dagger \mathbf{g}^\dagger \mathbf{U} \mathbf{U}^\dagger \mathbf{g} \mathbf{W}) = \text{Tr}(\mathbf{g}^\dagger \mathbf{g}). \quad (2.31)$$

Accordingly, the Frobenius norm provides a robust and physically meaningful target for training DeepPseudopot on EPC data, while avoiding spurious dependence on eigenvector phases or on the particular basis returned by the diagonalization within degenerate manifolds.

Overall, the training loss function includes contributions from the band structure (BS) mean-squared error, the deformation potential (defPot) mean-squared error, the electron-phonon coupling mean-squared error, and two optional penalties (**decay** or **mag-penalty**) that restrict unphysical behavior of the local pseudopotential.

$$\text{Loss} = \sum_{n\mathbf{k}} w_{n\mathbf{k}}^{BS} \left(E_{n\mathbf{k}} - \tilde{E}_{n\mathbf{k}} \right)^2 + \sum_i w_i^{\text{defPot}} \left(a_i^V - \tilde{a}_i^V \right)^2 \quad (2.32)$$

$$+ w^{EPC} \sum_{n \in VB} \sum_{m \in CB} |g_{nm\mathbf{k}\mathbf{q}}^{A\alpha}|^2 \quad (2.33)$$

$$+ \sum_{\alpha} w_{\alpha}^{\text{decay}} \int dG S(G; G_{\text{cut}}) |v_{\text{loc}}^{\alpha}(G)| \quad (2.34)$$

$$+ \sum_{\alpha} w_{\alpha}^{\text{mag}} \int dG S(|v_{\text{loc}}^{\alpha}(G)|; v_{\text{max}}^{\alpha}) \max(|v_{\text{loc}}^{\alpha}(G)| - v_{\text{max}}^{\alpha}, 0), \quad (2.35)$$

where $E_{n\mathbf{k}}$ and $\tilde{E}_{n\mathbf{k}}$ are the predicted and reference eigenvalues for band n at wavevector $\mathbf{k}$. a_i^V and $\tilde{a}_i^V$ are the predicted and reference deformation potential for transition i . $g_{nm\mathbf{k}\mathbf{q}}^{A\alpha}$ are the

EPC matrix elements. $S(x; x_0) = \frac{1}{1+e^{-k(x-x_0)}}$ is a shifted sigmoid function that is used to either smoothly penalizes non-decaying components of the local pseudopotential beyond a cut-off momentum, or the large magnitude local pseudopotential pieces. The first decay-penalty was used to enforce Fourier transform convergence from reciprocal to real space, while the mag-penalty eliminates highly oscillatory potential components that render the pseudopotential meaningless compared to all-electron calculations. $w_{n\mathbf{k}}^{BS}, w_i^{\text{defPot}}, w^{EPC}, w_{\alpha}^{\text{decay}}, w_{\alpha}^{\text{mag}}$ are tunable hyperparameters for balancing the loss function.

We also employed a growing-weight strategy within a curriculum-learning framework.[172, 173] In the initial stage of training, only the band-structure loss was assigned a nonzero weight, since fitting the reference GW band structure requires substantial optimization and typically induces the largest changes in the pseudopotential form. As the band-structure fit improved, we gradually increased the weights on bands near the conduction-band minimum (CBM) and valence-band maximum (VBM), as well as on $\mathbf{k}$ -points that are particularly important to the material’s electronic structure. This procedure places increasing emphasis on the accurate reproduction of band-edge physics relevant to nanomaterials. Once the band structure had reached satisfactory agreement with the reference data, we then increased the weights associated with the deformation-potential and EPC losses. These derivative properties become most meaningful after the equilibrium eigenvalue spectrum has already been captured. Empirically, introducing these additional loss terms generally does not lead to large further changes in the overall form of the DeepPseudopot. The decay-penalty term was typically kept active throughout training to enforce a physically reasonable reciprocal-space form of the DeepPseudopot. By contrast, the magnitude-penalty term was only introduced when the trained pseudopotential developed excessively large amplitudes, which could lead to highly oscillatory behavior in the near-core real-space potential.

2.4 Code package and software design principles

Modern computational materials research increasingly relies on complex software packages, making scientific software engineering practices essential for reproducibility, traceability, and long-term maintainability. During my PhD, I developed and extended several research codes spanning nanocrystal structure generation, filter diagonalization, Bethe-Salpeter Equation (BSE) workflows, and non-adiabatic coupling calculations. These experiences highlighted that scientific progress is often constrained not only by theory and algorithms, but also by whether the resulting code package implementations are modular, well-written, and easy to extend. In particular, a well-designed codebase enforces a clean separation between physical models, inputs, data, and execution, which supports version control, regression testing, and systematic feature development in the long run.

For DeepPseudopot, I developed the software infrastructure required to adapt semi-empirical pseudopotential theory to the machine learning setting, including training data preparation, model initialization, model optimization, validation and testing. The code package was designed explicitly with longevity and extensibility in mind. I intended to have

the code package easily support future physics-based extensions (e.g., new atomic environment descriptors, more flexible nonlocal or SOC function forms, electron-phonon training targets). I also implemented version control to distinguish model development from production, providing a stable API interface usable by internal group members and external collaborators alike.

DeepPseudopot is implemented primarily in Python, centered on NumPy/SciPy and PyTorch for numerical computing and deep learning. The codebase is organized around a small number of top-level modular implementations. The primary *training* entry point is `main.py`, which trains pseudopotential parameters from a bundle of input files, including system configuration and reference data. Parallelization was carefully implemented using a shared memory structure, and can be selected depending on user’s needs and compute setup. For streamlined evaluation and inference, `eval_fullBand.py` provides an alternative workflow that is specifically tuned for efficient evaluation of “full” band structures with hundreds of k -points. The primary implementation modules reside in `utils/`, which contains (i) readers for the input bundle, (ii) DeepPseudopot Hamiltonian construction and related utilities, (iii) neural-network model definitions, (iv) training loops, (v) Fourier transforms utilities, and (vi) visualization helpers. In addition, the repository includes dedicated regression and stress-test suites (e.g., `test_ham/`, `test_parallel/`, `test_memory/`) that check band structure and DeepPseudopot Hamiltonian construction fidelity, parallelization and multiprocessing correctness and performance, eigensolver stability, and memory scaling.

The modular code structure of DeepPseudopot mirrors the physical decomposition described throughout this chapter. Hamiltonian assembly is implemented as a composable pipeline that has swappable components of local pseudopotential terms, nonlocal projector terms and spin-orbit coupling contributions. On the other hand, the trainable components are encapsulated in model modules. This separation allows for systematic experimentation with model variants (e.g., swapping local representations, or enabling/disabling SOC/nonlocal channels), all while keeping the interfaces stable and consistent.

The repository also includes auxiliary tools for a growing list of common pre- and post-processing tasks. These include converting reference band structures from external electronic structure packages into the DeepPseudopot bundle format, generating real-space charge densities from plane-wave eigenvectors, densifying or sparsifying k -point paths, and analyzing a committee of learned pseudopotentials via clustering or dimensionality-reduction utilities.

Comprehensive user documentation, installation instructions, and tutorials are maintained online and serve as the reference for using and extending the software. The online manual describes the input bundle format (configuration files, k -point paths, band-weighting and loss definitions, reference band-structure files, and restart conventions), along with workflow recipes and troubleshooting guidance. Rather than duplicating the manual in this dissertation, I have provided a high-level architectural description and point readers to the online documentation and repository for implementation details and up-to-date usage examples.

The code repository and the online manual are publicly available at:

<https://github.com/TommyLinkl/DeepPseudopot>
<https://tommylinkl.github.io/DeepPseudopot>

In the next sections of this chapter, we present two representative case studies that demonstrate both the scientific capabilities of DeepPseudopot and the practical workflow enabled by the accompanying software package, including data preparation, model training, and downstream evaluation.

2.5 Si example

We first demonstrate the versatility and applicability of the DeepPseudopot model using silicon as a test case. Reference DFT+GW data for cubic diamond phase silicon were generated using the methods outlined in Section 2.3. Spin-orbit coupling effects were neglected, as they are known to be weak in Si. For the mean-field calculations, we used the Perdew-Burke-Ernzerhof exchange-correlation functional [174] with norm-conserving, scalar relativistic pseudopotentials as implemented in Quantum ESPRESSO. [175] A kinetic energy cutoff of 120 Ry was used, and the Brillouin zone was sampled using a Monkhorst-Pack $8 \times 8 \times 8$ $\mathbf{k}$ -point mesh in the self-consistent DFT calculation. The GW corrections were performed using the BerkeleyGW package within the single-shot G0W0 approximation. [57, 135, 176] The energy cutoff for the screened Coulomb interaction, as well as the number of bands used in the screened Coulomb and Coulomb-hole summations, were converged to ensure numerical accuracy. Additionally, we computed the deformation potentials for interband transitions $\Gamma_{15v} - \Gamma_{1c}$, $\Gamma_{15v} - X_{1c}$, $\Gamma_{15v} - L_{1c}$ at the same level of DFT+GW theory using a unit cell with $\pm 1\%$ isotropic deformation of the lattice constant.

The local pseudopotential for silicon was parameterized by a fully connected neural network with a single hidden layer containing 20 neurons and the Continuously Differentiable Exponential Linear Unit (CELU) activation function, [177] except in the output layer as described in Section 2.2. We used He initialization [178] to set the initial weights. To promote smooth behavior in reciprocal space, a small regularization term was included in the loss function to penalize nonzero components of the local pseudopotential beyond the momentum cutoff of 4.5 Bohr^{-1} .

The trained silicon machine-learned pseudopotential achieves high accuracy in reproducing reference electronic structure data, as illustrated in Fig. 2.2. The band structure predicted by the trained DeepPseudopot model closely matches the GW reference along the entire high-symmetry path, accurately capturing both energies and dispersions. To enhance accuracy at the band edges, the training loss function applied double weights to $\mathbf{k}$ -points at Γ , X and at the CBM along the $\Gamma - X$ path. As shown in Fig. 2.2(b), the resulting model reproduces interband transition energies at high-symmetry points with deviations of less than 0.050 eV. Notably, it predicts the fundamental band gap with exceptional precision: 1.136 eV from DeepPseudopot versus 1.137 eV from DFT+GW. In addition, the model

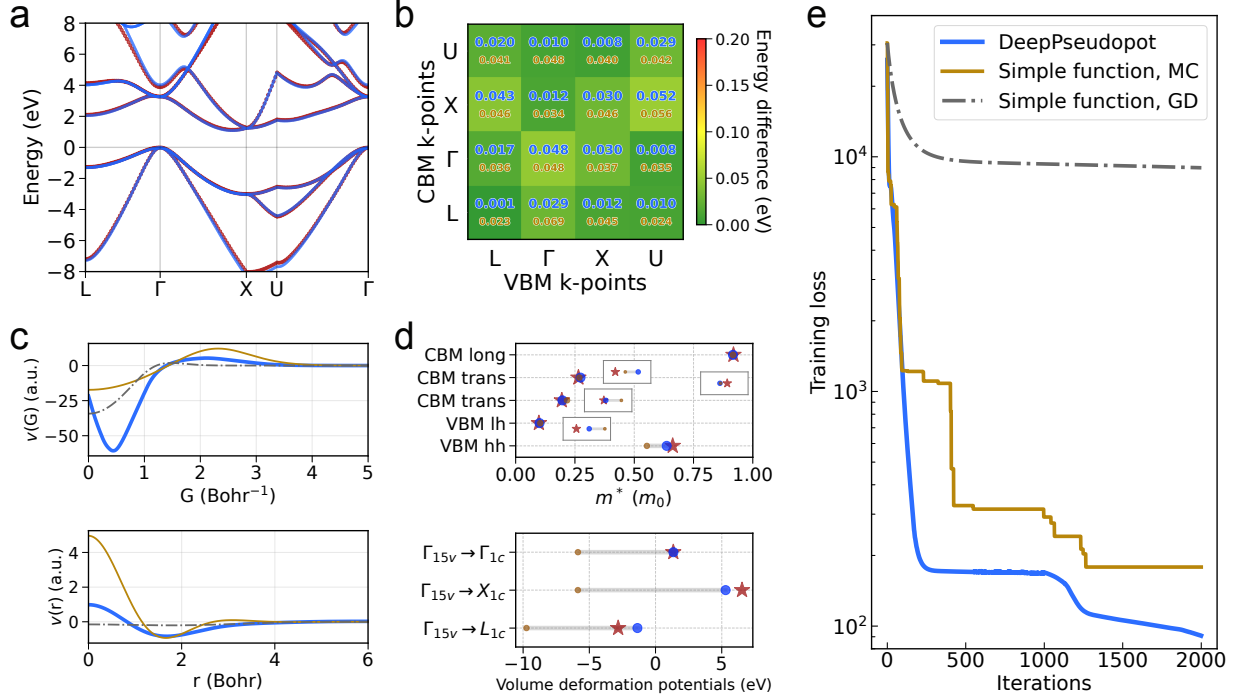


Figure 2.2: Band properties of silicon from training the DeepPseudopot model. The reference DFT+GW data (red), the DeepPseudopot model predictions (blue), and the simple functional form pseudopotential fitted using Monte Carlo sampling (yellow) are consistently color-coded across all panels. (a) Band structure of cubic diamond silicon. (b) Accuracy matrix for interband transition energies between high-symmetry points in the Brillouin zone. Grid colors and blue text show the absolute energy errors between reference values and the DeepPseudopot prediction. Yellow text shows the corresponding errors from the simple functional form pseudopotential for comparison. (c) Local pseudopotentials plotted in reciprocal space and real space. The simple functional form pseudopotential fitted using gradient descent is shown as grey dashed lines. (d) Effective masses (top) and deformation potentials (bottom). Insets show zoomed-in comparisons of effective masses. (e) Training loss evolution starting from a random initialization.

accurately reproduces effective masses and deformation potentials (see Fig. 2.2(d)), outperforming fits based on simple analytical forms of the local pseudopotential. This high level of agreement indicates that the model can faithfully capture the local electronic potentials, many-body interactions and perturbative properties in the prototypical Si system.

We also compared the training efficiency of the DeepPseudopot model against earlier semi-empirical pseudopotential frameworks. [108, 150] Traditional pseudopotentials typically used simple functional forms with only a few tunable parameters, which were adjusted

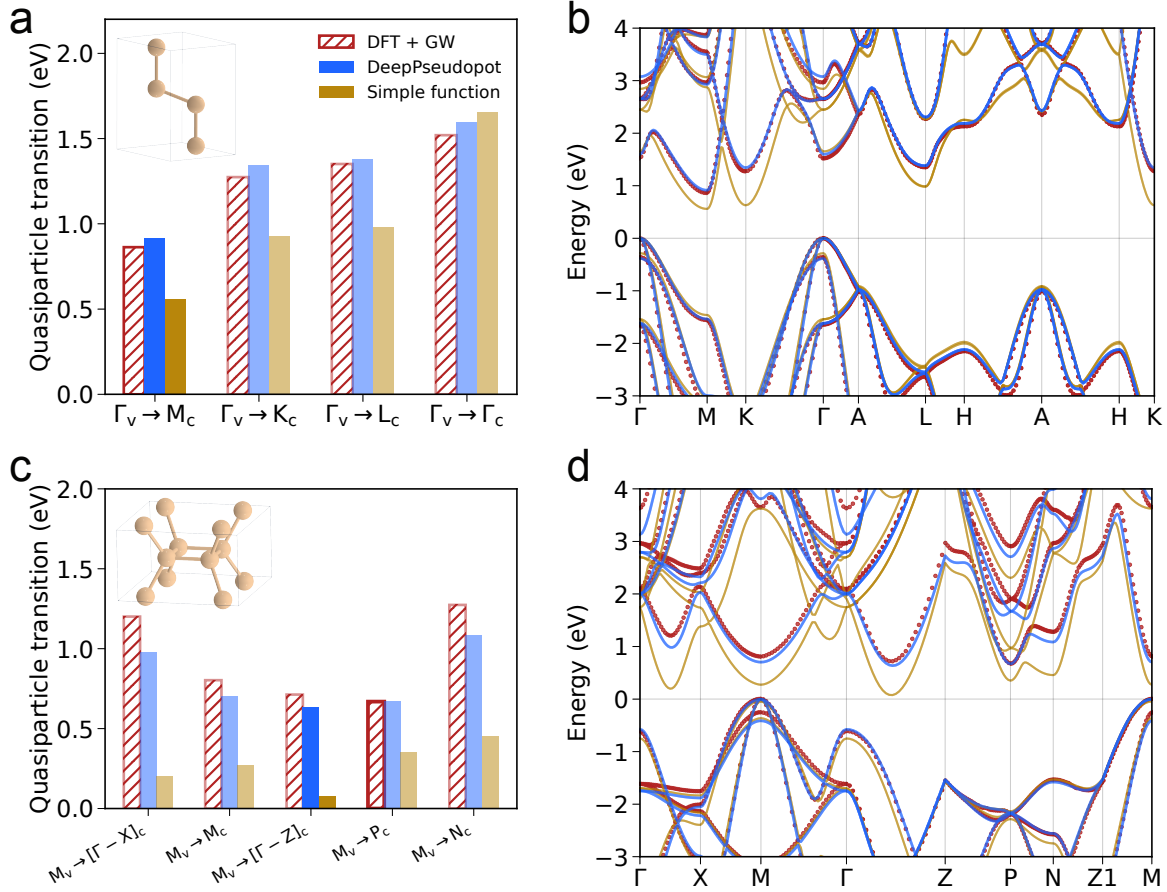


Figure 2.3: DeepPseudopot model predictions for the hexagonal diamond (lonsdaleite) and body-centered tetragonal (bct) structures of silicon. Consistent with Figure 2.2, reference DFT+GW data are shown in red, DeepPseudopot model predictions in blue, and simple functional form pseudopotentials in yellow. (a) The interband transition energies between the valence band maximum and various $\mathbf{k}$ -points of the conduction band edge in the lonsdaleite structure. The fundamental band gaps are highlighted. (b) The reference and predicted band structures of the lonsdaleite structure. (c, d) Same as panels (a) and (b), but for the bct structure.

to reproduce band energies. Despite the small parameter space, prior work often relied on stochastic sampling techniques such as Monte Carlo sampling, due to the rugged parameter landscape and the complexity of the eigenvalue operator. To benchmark training performance, we implemented both Monte Carlo (MC) and gradient descent (GD) optimization for the simple functional form, which uses the numerical back-propagation implementation via PyTorch. A common random initialization was selected, with the DeepPseudopot model

first trained to reproduce the same initial pseudopotential function as the other two methods to ensure a fair comparison. As depicted in Fig. 2.2(e), the DeepPseudopot model illustrates improved efficiency, needing fewer iterations of band structure evaluations for a comparable fit. It achieves comparable error levels to MC with less than one-fifth of the computational cost, due to its flexible representation enabling better optimization with respect to the input data.

In contrast, GD on the simple functional form often becomes trapped in a suboptimal local minimum, while MC improves the fit but remains slower and less accurate than DeepPseudopot. Given the empirical nature of the training process and the complexity of the loss landscape, the advantage of DeepPseudopot is robust across runs, but the relative improvement varies with the random initialization. Although demonstrated here for the simple silicon system, the efficiency and flexibility of DeepPseudopot become increasingly important for more complex unit cells. The ability to reach a better fit, reflected in a lower minima of the loss function is critical for achieving the high transferability required of machine-learned pseudopotentials, as demonstrated below.

The trained DeepPseudopot model not only reproduces GW-level reference band properties and deformation potentials at high accuracy within the cubic diamond (cd) phase used for training, but also demonstrates great transferability to other silicon allotropes, as shown in Fig. 2.3. To assess the model’s predictive performance on unseen structures, we applied it to two additional semiconducting phases of silicon: the hexagonal diamond (lonsdaleite) structure and the body-centered tetragonal (bct) structure, both of which have been studied theoretically or experimentally in literature. [179, 180] While these lattice structures preserve four-fold silicon atom coordination, they exhibit different bond lengths and local atomic environments compared to the cd structure. These structural variations present interesting cases for assessing the model’s transferability.

In both the lonsdaleite and bct structures, the DeepPseudopot model accurately reproduces the GW band dispersions and fundamental band gaps, as shown in Fig. 2.3. The predicted transition energies between the VBM and the CB edges at various $\mathbf{k}$ -points deviate by less than 0.150 eV from the GW reference. For comparison, we also computed the band structures using the traditional pseudopotential based on simple analytical functional forms, as trained using MC sampling in Fig. 2.2(e). Although both models achieved comparable training loss within the cd phase, the more flexible DeepPseudopot model consistently outperforms the simple functional form pseudopotential in prediction tasks on unseen allotropes. The latter severely underestimates the band gaps and misrepresents band dispersions and crossings in the lonsdaleite and bct phases (see Fig. 2.3(b) and (d)).

However, we note that this level of generalizability without additional retraining or explicit inclusion of atomic environment in the model is not guaranteed across more complex materials and most likely succeeds here due to the relative simplicity of the silicon phases and the similarity between the lonsdaleite, bct, and cd structures. One example where DeepPseudopot shows limited transferability is in the conduction band minimum (CBM) prediction for the bct structure. In the GW reference calculation, the CBM of the bct structure is located at the P point, with a competing minimum along the $\Gamma - Z$ path only 0.044 eV

higher in energy. In contrast, the DeepPseudopot prediction incorrectly identifies the CBM along the $\Gamma - Z$ path (see Fig. 2.3(c)), showing the challenges of resolving very small energy differences without explicit retraining. Furthermore, the current model would not be expected to transfer well to amorphous silicon, where the local atomic environments differ significantly, including variations in silicon coordination numbers. To systematically improve transferability, one can expand the training set to include more phases, [46] enabling the flexible machine-learned local pseudopotential to efficiently extrapolate across diverse structural environments.

2.6 III-V example

The SEPM has been widely fitted across multiple crystal structures—such as wurtzite and zinc blende CdSe [158, 160]—but its ability to generalize across alloyed systems is less explored. Here, we show how training a DeepPseudopot model on a set of four group III-V semiconductor compounds provides accurate route to the electronic and vibronic properties of binary-compound and ternary-alloyed nanoscale crystal systems in comparison to experimental measurements.

The model was trained on DFT+GW quasiparticle band structures and deformation potentials of InAs, InP, GaAs, and GaP, prepared using the procedures described in the Methods section 2.3. Importantly, spin-orbit coupling was explicitly included in the reference calculations, and each band structure was statically shifted to ensure consistent band alignment across materials. To enable transferability to alloyed systems, each elemental pseudopotential (cation or anion) was shared across the two compounds in which the element appears, without interpolation or compound-specific tuning.

GW band structure training data of InAs, InP, GaAs, and GaP were prepared following the methods outlined in Section 2.2, using procedures similar to those described for silicon in Section 2.5, with several important distinctions. Among these III-V semiconductors, heavier elements such as In and As are known to lead to significant SOC effects. To ensure consistency, fully relativistic pseudopotentials were employed for all elements in the DFT calculations. In the case of InAs, due to the small fundamental gap, DFT calculation using the PBE functional yields a semi-metallic system. Thus, we performed a second iteration of the screened exchange summation using updated G0W0 quasiparticle energies to correctly account for state occupations. [181] Given that the model was trained across multiple compounds and will be applied to nano-heterostructures, consistent band alignment was essential. We statically shifted each band structure so that its VBM aligns with its experimental work function. [182] Deformation potentials were computed using the same procedure and included in the training dataset.

The DeepPseudopot model was constructed with one hidden layer of 50 neurons and the CELU activation function, with four outputs corresponding to the local pseudopotentials of P, Ga, As, and In. Four accompanying SOC parameters were also included and initialized randomly. Each elemental pseudopotential (cation or anion) was shared between the two ma-

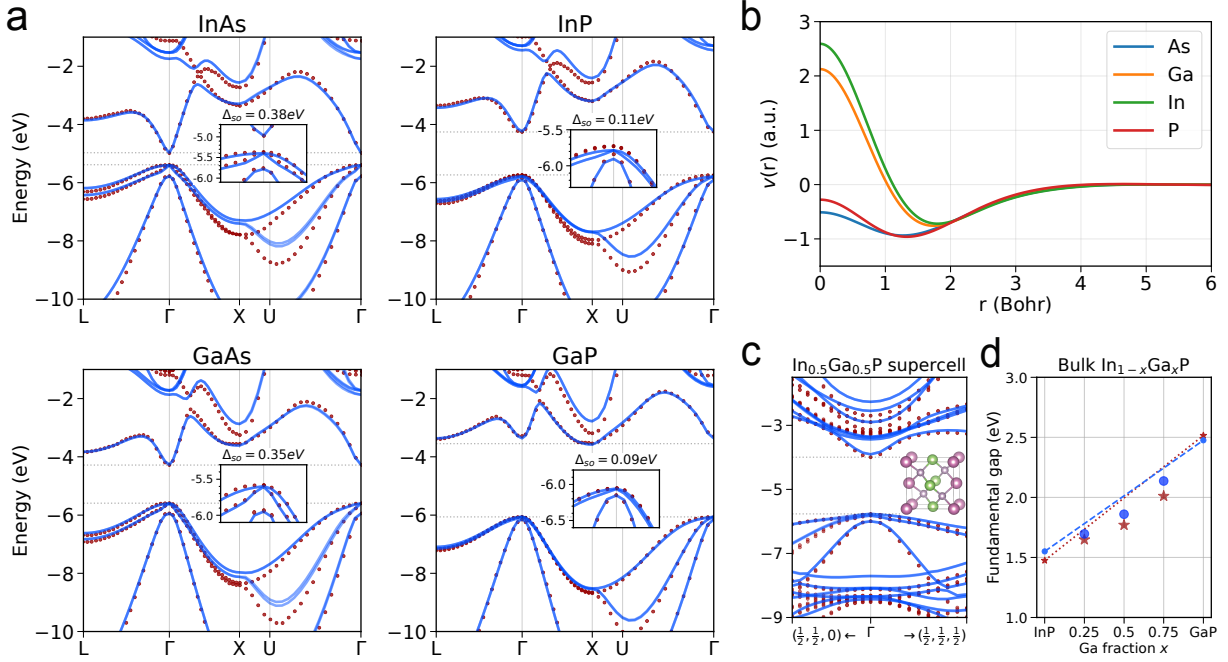


Figure 2.4: Band properties of group III-V semiconductors from training the DeepPseudopot model. Reference DFT+GW data are shown in red throughout; predictions from the trained DeepPseudopot model are shown in blue. (a) Band structures of InAs, InP, GaAs, GaP, from the trained DeepPseudopot model (blue lines) compared to GW reference (red dots). Insets show zoomed-in views around the VBM, highlighting the spin-orbit splitting energy. (b) Real-space local pseudopotentials for each element. (c) Predicted band structure of alloyed $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ around the Γ point. The inset shows the 8-atom zincblende conventional cell with cation substitutions used in the calculation. Atom colors: Pink-In, Green-Ga, Purple-P. (d) Fundamental band gaps of bulk $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy supercells.

terials in which the element appears, without any interpolation across systems. This design is particularly important for modeling alloyed systems. To prioritize accurate reproduction of band-edge physics, the loss function used to train the DeepPseudopot model was heavily weighted towards bands near the gap, the spin split-off bands at Γ point, and Γ , X and L points in the Brillouin zone.

As shown in Fig. 2.4, the trained DeepPseudopot model reproduces the band-edge electronic structure of the four III-V semiconductors with high fidelity. To quantify this agreement, we compared the quasiparticle transition energies between the valence-band maximum (VBM) and the conduction-band edges at Γ , X , and L , together with the spin-orbit splittings. These band-edge quantities are particularly important for predicting alloy behavior. In particular, GaP differs from the other three compounds in having its conduction-band

minimum at X rather than at Γ , and its conduction-band edges at Γ , X , and L lie close in energy. This near-degeneracy enables direct-to-indirect gap transitions in III-V alloys involving GaP. Across all four materials, DeepPseudopot reproduces the band-edge transition energies and spin-orbit splittings with errors below 0.080 eV, with most band-edge transitions falling below 0.050 eV. These results are summarized in Fig. 2.5.

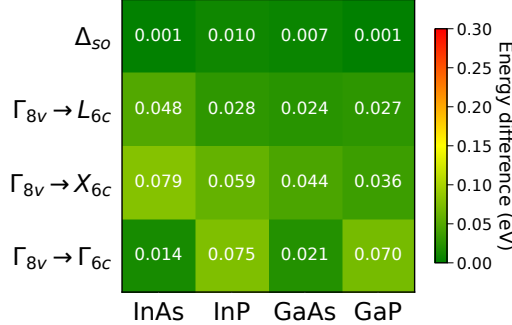


Figure 2.5: Accuracy matrix for DeepPseudopot predictions of interband transition energies in group III-V semiconductors. The materials are labeled along the horizontal axis, and the transition energies and spin-orbit splittings are labeled along the vertical axis. The grid colors and numerical values indicate the energy deviations between DeepPseudopot and the reference GW calculations.

The somewhat larger deviations observed for higher conduction bands, relative to the silicon case, are a direct consequence of the loss-function design. During training, we assigned substantially greater weight to the highest valence bands, lowest conduction bands, and spin-split-off bands, while de-emphasizing deeper valence and higher conduction states. This prioritization was motivated by the intended applications of DeepPseudopot to nanocrystal optoelectronics, where optical excitations are dominated by electron-hole pairs formed near the band edges. The resulting model therefore emphasizes the physically relevant low-energy electronic structure while maintaining good accuracy over the broader band manifold. To our knowledge, this is the first unified construction of atomistic pseudopotentials, including spin-orbit coupling, for Ga, In, P, and As across this set of III-V semiconductors.

Band identity is not explicitly tracked in either the training data or the model output; rather, the bands are ordered only by energy at each $\mathbf{k}$ -point. As a consequence, genuine band crossings may appear visually as avoided crossings in the plotted dispersions, particularly among the higher conduction bands in Fig. 2.4(a). This limitation, however, does not compromise the physical character of the underlying states. To assess the quality of the predicted eigenvectors, we computed the band-resolved charge density for a representative material, GaP, and compared it with DFT. The charge density associated with band n is

given by

$$\rho_n(\mathbf{r}) = \int_{\text{BZ}} d^3\mathbf{k} |\psi_{n\mathbf{k}}(\mathbf{r})|^2. \quad (2.36)$$

As shown in Fig. 2.6, the DeepPseudopot charge density reproduces the qualitative spatial features and symmetries of the DFT result, despite some quantitative differences. This agreement gives confidence that the learned wavefunctions are sufficiently reliable for subsequent Bethe-Salpeter equation calculations. In Fig. 2.4(b), we further visualize the learned local pseudopotentials in real space, where clear chemical trends emerge: the two cation potentials resemble one another, as do the two anion potentials, consistent with their underlying chemical similarity.

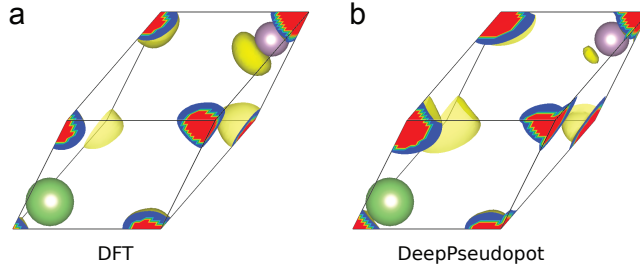


Figure 2.6: Valence-band charge density of GaP within a single unit cell, calculated using (a) DFT@PBE and (b) DeepPseudopot. Gallium atoms are shown in green and phosphorus atoms in purple.

To assess the transferability of the trained DeepPseudopot model beyond its training set, we tested its predictions on bulk III-V alloys. Specifically, we constructed 8-atom zincblende conventional cells of $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloys at simple fractional compositions ($x = 0.25, 0.5, 0.75$), which represent the smallest special quasirandom structures commensurate with the stoichiometry. [183, 184] Each alloy supercell was relaxed prior to band structure calculations near the Γ point. Despite the absence of explicit In-Ga-P interactions in the training data, the predicted band structures from the DeepPseudopot model closely match the GW reference (see Fig.2.4c), and the fundamental band gaps across $\text{In}_{1-x}\text{Ga}_x\text{P}$ compositions qualitatively reproduce ab initio trends with very small errors (see Fig.2.4d). This test on bulk alloys demonstrates the model’s ability to generalize beyond the training set of binary semiconductor primitive cells and accurately capture electronic structures of bulk alloy supercells, thanks to its physically motivated Hamiltonian design and elemental sharing parametrization.

2.7 DeepPseudopot from nanocrystals to molecular systems

As shown in the sections above, DeepPseudopot has demonstrated strong performance as a machine-learned generalization of traditional semi-empirical pseudopotential theory, enabling accurate and scalable predictions of solid-state and nanomaterial electronic properties, including band structures, optical response, and charge densities. In particular, the framework has proven effective for modeling the optoelectronic properties of semiconducting materials.

Despite these successes, important challenges remain that limit the applicability of the current formulation. The first area for improvement concerns the treatment of surface ligands in colloidal nanocrystals. In prior work, passivation ligands have been modeled using a fictitious Gaussian-type pseudopotential that smoothly truncates the total potential in real space. While this approximation captures overall size-related quantum confinement effects, it fails to model the specific ligand types or the detailed atomic structure of ligands. As a result, it cannot describe how ligand identity, coverage, orientation, or thermal fluctuations influence optoelectronic properties, while ligands have been widely observed to have a significant impact in experiments. One specific area of interest is to model phenomena such as ligand-induced chirality and the circular dichroism spectroscopy in nanocrystals.

A second limitation arises from model transferability. Although DeepPseudopot generalizes well across various crystalline phases and compositionally uniform alloys that are not present in the training data, its performance degrades in systems with strong local heterogeneity, including point defects, impurities, and amorphous structures. This behavior reflects the broader challenge of generalizability across diverse local chemical environments that is shared by many machine-learning models.

Together, these limitations motivate the development of a more general and environment-aware machine-learned pseudopotential framework. To this end, we extend DeepPseudopot by incorporating symmetry-preserving atomic environment descriptors that encode the local structural information and serve as inputs to the neural network. This extension is paired with datasets prepared with local distortions to the materials. The explicitly encoded local structural information enables treatment of ligands and molecular systems, while preserving the overall structure of the original Hamiltonian.

We retain the central structure of the original DeepPseudopot Hamiltonian while allowing each atomic pseudopotential to depend explicitly on its local chemical environment. In the original formulation, the local pseudopotential associated with atom α is represented as a learned function of the reciprocal-space separation $|\mathbf{G}_i - \mathbf{G}_j|$, which provides an efficient and transferable description for chemically homogeneous systems. Here, we generalize this construction by conditioning the atomic pseudopotential on an additional descriptor embedding that encodes the local arrangement of neighboring bonded atoms around each nuclear center, as illustrated in Fig. 2.7. The resulting framework preserves the physically motivated decomposition of the quasiparticle Hamiltonian while introducing the flexibility needed to distinguish different local bonding environments.

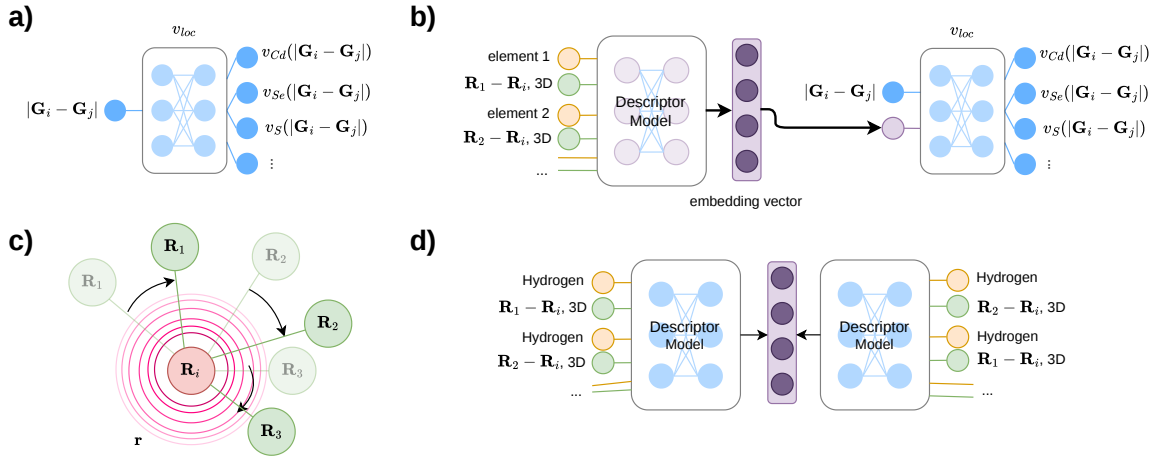


Figure 2.7: Schematic illustration of the environment-dependent extension to the DeepPseudopot framework and symmetry preservation requirements. (a) The original DeepPseudopot model, where the pseudopotential is represented as a function of the reciprocal-space separation $|\mathbf{G}_i - \mathbf{G}_j|$. (b) Environment-dependent extension of DeepPseudopot, in which a descriptor model maps the local nuclear environment to an embedding vector that conditions the pseudopotential model. (c) Rotational invariance requirement of the local environment descriptor in DeepPseudopot. (d) Permutation invariance requirement of the local environment descriptor with respect to bonded atoms of the same element.

For systems containing both inorganic semiconductor atoms and organic ligand atoms, we write the quasiparticle Hamiltonian as

$$\hat{h}_{qp} = \hat{t} + \sum_{\alpha \in \text{inorganic}} [\hat{v}_{loc}^{\alpha} + \hat{v}_{nonloc}^{\alpha} + \hat{v}_{soc}^{\alpha}] + \sum_{\beta \in \text{organic}} \hat{v}_{loc}^{\beta}, \quad (2.37)$$

where $\hat{t}$ is the kinetic-energy operator, and the inorganic atoms retain the local, nonlocal, and spin-orbit pseudopotential terms introduced in the preceding sections. In the present proof-of-concept implementation, we focus on learning environment-dependent local pseudopotentials for ligand atoms. For an atom-centered potential associated with nucleus β , we write

$$v_{loc}^{\beta} = v_{loc}^{\beta}(|\mathbf{r} - \mathbf{R}_{\beta}|; d_{\beta}), \quad (2.38)$$

where $\mathbf{R}_{\beta}$ is the nuclear coordinate and d_{β} is a learned descriptor embedding of the local neighborhood surrounding atom β . The descriptor embedding is constructed from the relative coordinates of atoms within a finite cutoff centered on β ,

$$d_{\beta} = f(\{\mathbf{R}_m - \mathbf{R}_{\beta} \mid m \in \mathcal{N}_{\beta}\}), \quad (2.39)$$

where $\mathcal{N}_\beta$ denotes the set of neighboring atoms included in the local environment. In practice, this descriptor must satisfy several symmetry requirements. First, translational invariance is enforced naturally by using relative coordinates rather than absolute positions. Second, because the local pseudopotential is retained in an atom-centered radial form, the descriptor should be rotationally invariant, so that equivalent environments differing only by rigid rotation yield the same conditioned potential. Third, the descriptor must be permutation invariant with respect to neighboring atoms of the same element, ensuring that relabeling chemically equivalent atoms does not alter the predicted potential. These symmetry constraints are essential for obtaining a physically meaningful and data-efficient representation, and are illustrated schematically in Fig. 2.7(c,d). In this work, we use atom-centered environment descriptors, particularly smooth overlap of atomic positions (SOAP), [185] that satisfy these requirements and map each local neighborhood to a fixed-dimensional embedding, independent of the number of atoms in the neighborhood.

An important modeling choice is that we continue to represent each atomic local pseudopotential as spherically symmetric with respect to its own nuclear center. At first glance, this may appear restrictive for molecules and ligand-coated nanocrystals, where bonding is strongly anisotropic. However, the quantity of physical interest is not the isolated atomic potential itself, but the total potential,

$$V_{loc}(\mathbf{r}) = \sum_{\beta} v_{loc}^{\beta}(|\mathbf{r} - \mathbf{R}_{\beta}|; d_{\beta}), \quad (2.40)$$

which is generally not spherically symmetric once contributions from all atoms are superposed. In this construction, anisotropy enters implicitly through the environment-dependent conditioning of the atom-centered potentials. Each atomic pseudopotential therefore becomes one member of a family of radial functions indexed by the local bonding geometry, rather than a single universal function for a given element. This design preserves the computational and conceptual simplicity of the original pseudopotential framework while introducing sufficient flexibility to capture local chemical heterogeneity.

As an initial validation, we apply the environment-dependent DeepPseudopot framework to the H_2 molecule, which provides the simplest setting in which local geometry and bond stretching can be cleanly isolated. We emphasize that H_2 is used here as a controlled benchmark rather than as a realistic ligand model. The ultimate goal is to treat chemically realistic ligand molecules and ligand-semiconductor interfaces, where the local environment plays a central role in determining the electronic structure. Nevertheless, H_2 provides a stringent proof-of-concept for testing whether the model can learn environment-dependent pseudopotentials, reproduce the variation of single-particle energies under structural distortion, and capture the associated electron-phonon couplings.

For this benchmark, we generate reference data at the restricted Hartree-Fock (RHF) / cc-pVTZ level of theory. Because the objective here is to test the machine-learned pseudopotential architecture rather than to establish the ultimate electronic-structure accuracy for H_2 , this level of theory is sufficient for a first demonstration. The H-H separation is sampled over the range 0.6-0.9 Å, which spans the thermally accessible region around the

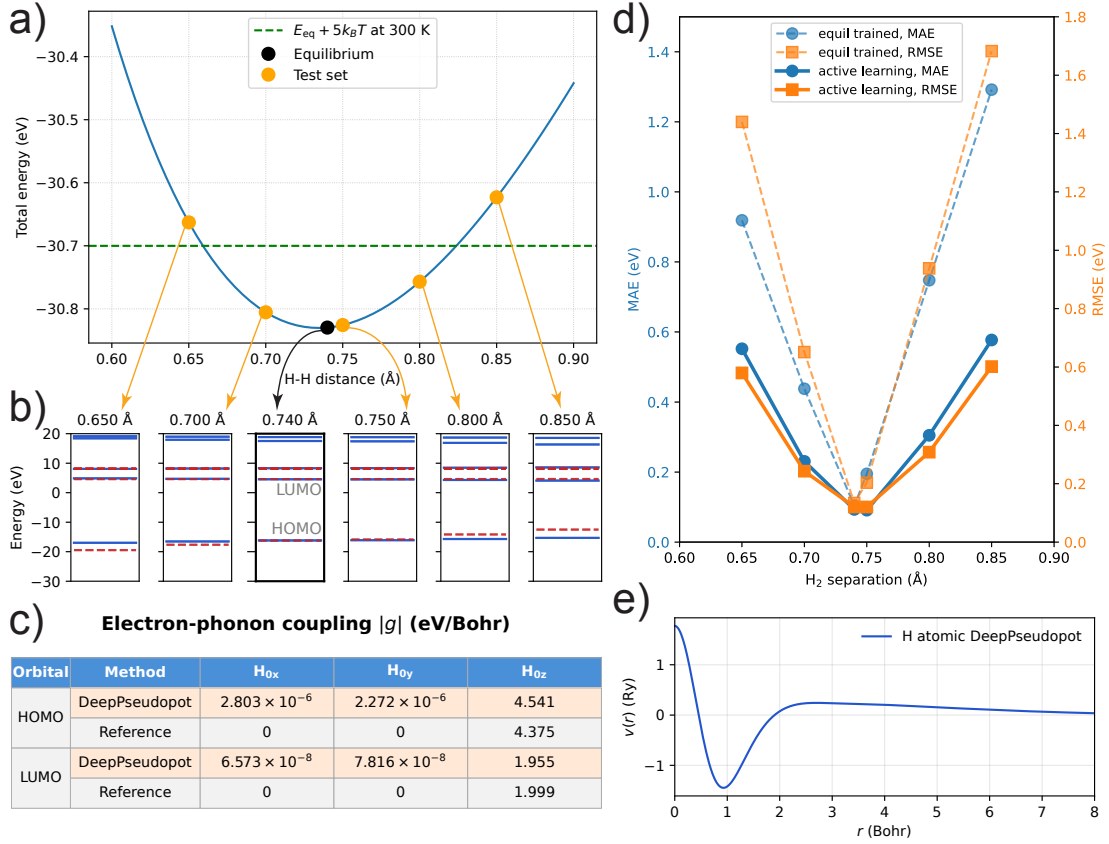


Figure 2.8: Environment-dependent DeepPseudopot results for the H₂ molecule. (a) Ground-state potential energy curve of the H₂ molecule as a function of H-H bond length, with the equilibrium geometry (black dot), the thermal window defined by $5k_B T$ at 300 K (green dashed line), and the selected test configurations (orange dots) indicated. (b) Molecular orbital energies at different H-H separations, comparing the HOMO, LUMO, and LUMO+1 energies predicted by DeepPseudopot (blue lines) with those from reference *ab initio* calculations (red dashed lines), showing good agreement in the thermally accessible region near equilibrium. (c) Comparison of electron-phonon coupling magnitudes $|g|$ for the HOMO and LUMO between the trained DeepPseudopot model and the reference calculations. (d) MAE and RMSE of the HOMO, LUMO, and LUMO+1 energies for DeepPseudopot models trained only at the equilibrium configuration and improved using active learning. (e) Atomic pseudopotential of hydrogen in the DeepPseudopot model.

equilibrium bond length, as shown in Fig. 2.8(a). We focus first on three frontier molecular orbitals, namely the HOMO, LUMO, and LUMO+1, which already covers an energy range of ~ 30 eV energy. We also neglect nonlocal and spin-orbit terms in this first implementation. In addition to orbital energies, we also train against electron-phonon coupling matrix

elements obtained from *ab initio* calculations.

We first consider a minimal training strategy in which the model is trained only at the equilibrium H_2 geometry. Remarkably, even this extremely limited training set is sufficient to reproduce the orbital energies at the training point essentially exactly and to provide reasonable predictions for nearby distorted configurations. As shown in Fig. 2.8(b) (“equil trained” curves), the model captures the evolution of the HOMO, LUMO, and LUMO+1 energies with bond stretching with good accuracy in the vicinity of equilibrium. The same model also reproduces the dominant electron-phonon coupling magnitudes for the HOMO and LUMO with encouraging accuracy, as summarized in Fig. 2.8(c). These results indicate that the environment-dependent extension can encode not only the static electronic structure but also the first-order derivative of the electronic Hamiltonian with respect to nuclear motion.

The limitations of the equilibrium-trained model become apparent as the H-H separation moves further away from equilibrium. In particular, prediction errors increase rapidly outside the local thermal window, reflecting the fact that a single geometry is insufficient to constrain the pseudopotential over a broader region of configuration space. To address this issue, we adopt a simple active-learning strategy. Configurations with large prediction errors are identified, added to the training set, and the model is retrained. With only a few additional bond lengths near equilibrium (0.741, 0.71, 0.81 Å), the errors in the frontier orbital energies decrease substantially across the sampled range, as shown in Fig. 2.8(d). This improvement is obtained with minimal additional data and modest retraining, illustrating that the environment-dependent DeepPseudopot framework is naturally compatible with iterative data acquisition strategies. Such an approach will be especially valuable for realistic ligand and interfacial systems, where exhaustive sampling of all relevant local geometries is impractical. Finally, the learned atomic hydrogen pseudopotential shown in Fig. 2.8(e) remains smooth and physically reasonable, further supporting the internal consistency of the model.

Although the present benchmark is intentionally simple, it establishes several key points. Atom-centered environment descriptors can be incorporated into DeepPseudopot without abandoning the original Hamiltonian structure. The resulting model can describe geometry-dependent orbital energies and electron-phonon couplings in a molecular system. Furthermore, active learning provides a practical route to extend the model across relevant regions of structural phase space without requiring dense *ab initio* sampling from the outset.

Several extensions remain for future work. Most importantly, the present demonstration includes only environment-dependent local pseudopotentials; incorporating environment-aware nonlocal and spin-orbit components will be important for realistic chiral surface chemistries. In addition, isolated H_2 does not capture the complexity of ligand binding, surface reconstruction, or semiconductor-ligand hybridization. A more complete implementation will therefore require training on realistic ligand molecules, adsorbed ligand-surface geometries, and thermally distorted nanocrystal interfaces, ideally using periodic first-principles calculations (such as hybrid DFT or GW) and broader configurational sampling. These developments will enable a unified pseudopotential framework in which inor-

ganic cores, organic ligands, and their interfaces are treated on the same footing, opening the door to predictive modeling of ligand-dependent optoelectronic phenomena in colloidal nanomaterials.

2.8 Conclusions

We developed DeepPseudopot, a machine-learning atomistic semi-empirical pseudopotential surrogate model capable of reproducing DFT+GW-level electronic structure properties with very high precision across a diverse set of elemental and compound semiconductors. The model combines a flexible neural network architecture of the local screened pseudopotentials with analytically tractable non-local and spin-orbit coupling terms to capture angular-momentum-dependent and relativistic effects. Physically motivated design choices—including species-specific potential sharing without interpolation, reciprocal-space decay regularization, and targeted loss function weighting at key bands and $\mathbf{k}$ -points—enable accurate description of band-edge physics, including quasiparticle energies, deformation potentials, and effective masses.

Beyond the periodic bulk setting, we further extended the framework to incorporate local atomic environment descriptors of bonded nuclei, enabling the treatment of systems without periodic boundary conditions within the same atomistic pseudopotential formalism. Preliminary demonstrations on simple molecular systems establish the feasibility of this strategy and motivate future applications to realistic ligand molecules, ligand-semiconductor interfaces, and other chemically complex nanoscale systems. In parallel, we developed an open-source software package that integrates DeepPseudopot model construction, training, and nanoscale electronic structure workflows, providing a solid foundation for continued method development and adoption by the broader research community.

Applied to silicon and group III-V semiconductors (InAs, InP, GaAs, GaP), DeepPseudopot achieves quantitative agreement with GW reference data and significantly outperforms traditional analytic semi-empirical pseudopotentials in both accuracy and training efficiency. The model was shown to generalize well to unseen crystal phases, bulk alloys, large nanostructures, as well as alloyed nanostructures, capturing essential features of electronic, optical, and vibronic properties with no additional retraining. This showcases that the DeepPseudopot model can learn very efficiently from only a small dataset of bulk band structures and deformation potentials, then directly applied to perform transferable, highly accurate electronic structure calculations for large nanoscale systems at a fraction of the computational cost of the reference theory. DeepPseudopot is thus positioned as a broadly applicable tool for the data-driven design and discovery of complex nanomaterials with tailored properties.

Despite accurately describing silicon and III-V alloys, several areas in DeepPseudopot require further development. The non-local and SOC terms are currently confined to one angular momentum channel and are represented by simple analytical functions with limited tunable parameters, a design choice necessitated by the high computational cost of evaluating these terms in the spinor plane wave basis. Developing more efficient algorithms for

constructing these matrices could enable higher angular momentum projections and allow for flexible neural network representations. Additionally, relaxing the assumption of spherical symmetry in the local term could further improve DeepPseudopot by allowing for a more flexible representation of the local potential. [46] Furthermore, the current local pseudopotential lacks explicit long-range treatment,[38] which, while sufficient for capturing bulk deformation potentials and exciton-phonon coupling in nanocrystals, may not accurately model Frohlich-type electron-phonon interactions.[128] These developments would broaden DeepPseudopot’s applicability to a wider range of materials, and will be the subject of future development.

Chapter 3

Excited state photophysics of colloidal III-V nanocrystals

This chapter includes material adapted from the following published articles:

- Justin C. Ondry, Zirui Zhou, Kailai Lin, Aritrajit Gupta, et al. **“Reductive pathways in molten inorganic salts enable colloidal synthesis of III-V semiconductor nanocrystals,”** *Science* 386, 401–407 (2024). [80] Adapted for dissertation use in accordance with AAAS author reuse policy.
- Kailai Lin, Dipti Jasrasaria, Jason J. Yoo, Mounqi Bawendi, Hendrik Utzat, and Eran Rabani. **“Theory of Photoluminescence Spectral Line Shapes of Semiconductor Nanocrystals,”** *The Journal of Physical Chemistry Letters* 14(32), 7241–7248 (2023). [127] Adapted with permission. Copyright 2023 American Chemical Society.
- Aritrajit Gupta, Justin C. Ondry, Kailai Lin, et al. **“Composition-Defined Optical Properties and the Direct-to-Indirect Transition in Core-Shell $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ Colloidal Quantum Dots,”** *Journal of the American Chemical Society* 145(30), 16429–16448 (2023). [79] Adapted with permission. Copyright 2023 American Chemical Society.
- Jun Hyuk Chang, Danial Zangeneh, Heng-Chi Chu, Justin C. Ondry, Kailai Lin, et al. **“Emissive Colloidal GaAs Quantum Dots,”** *Journal of the American Chemical Society*, in press (2026). [186] Adapted with permission. Copyright 2026 American Chemical Society.

As discussed in Chapter 1, advances in molten-salt chemistry have enabled the colloidal synthesis of high-quality binary and alloyed III-V nanocrystals, opening a long-standing opportunity for systematic investigation of their excited-state electronic structure and photophysics under quantum confinement. While the bulk optoelectronic properties of III-V semiconductors are extensively characterized, far less is understood about how excitonic

structure, radiative recombination dynamics, exciton-phonon coupling, and band-edge character evolve in the strongly confined nanocrystal regime. The availability of a generalizable synthetic platform based on molten-salt redox chemistry, capable of producing GaAs, GaP, and composition-tunable $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals with independent control over size and composition now enables direct, quantitative comparison between atomistic theory and experiment.

In this chapter, we investigate the excited-state properties and photophysics of colloidal III-V nanocrystals using atomistic modeling, and leverage this newly accessible materials platform to validate the theoretical framework against experiment. More broadly, this chapter aims to establish how atomistic electronic-structure theory can be used not only to reproduce measured optical observables, but also to reveal the microscopic origin of radiative and vibronic phenomena in quantum-confined III-V systems.

Section 3.1 focuses on GaAs and related binary III-V semiconductor nanocrystals as a foundation for this analysis. Within the unified DeepPseudopot framework, we compute optical gaps, shape-dependent electronic and optical properties, radiative lifetimes, exciton-phonon coupling strengths, and Stokes shifts, and compare these predictions with available experimental measurements. This section establishes the binary III-V nanocrystal as a benchmark system for connecting atomistic electronic structure to ensemble optical properties.

Section 3.2 then develops an atomistic linear-response framework for simulating phonon-resolved photoluminescence from single nanocrystals. We first validate this approach using well-characterized CdSe/CdS quantum dots, where detailed single-particle spectroscopic data provide a stringent benchmark, and then apply the same framework to GaAs nanocrystals. This enables direct interpretation of fluorescence line narrowing (FLN) and photoluminescence excitation (PLE) measurements in terms of the underlying excitonic structure, phonon modes, and exciton-phonon couplings.

Section 3.3 extends the analysis to ternary III-V alloys, with particular emphasis on GaP-containing systems and composition-tuned band-edge character. Although crystal momentum ($\mathbf{k}$) is not strictly defined in finite nanocrystals, we show that it remains a useful and physically meaningful descriptor of electronic structure in quantum-confined alloys. This framework allows us to connect the bulk direct-to-indirect crossover to composition-dependent wavefunction character, oscillator strength, and experimentally observable photophysics in alloyed nanocrystals.

Finally, Section 3.4 summarizes the main conclusions of the chapter and outlines future directions.

3.1 Exciton energies and optical transitions of GaAs, InP, InAs, GaP QDs

Upon optical excitation of semiconductor nanocrystals, correlated electron-hole pairs, or excitons, form as the fundamental photoexcited quasiparticles. Their binding energies, fine structure, transition strengths, and coupling to phonons govern experimentally observable quantities such as optical gaps, oscillator strengths, radiative lifetimes, emission spectra, and Stokes shifts. In this section, we first describe the methods used to compute these excitonic properties within the atomistic DeepPseudopot framework, including the quasiparticle Hamiltonian, Bethe–Salpeter equation, and exciton–phonon coupling. We then present results for binary III–V nanocrystals, with particular focus on GaAs quantum dots.

The geometries of QDs were constructed by cutting target shapes and sizes from bulk zinc blende lattices, followed by structural relaxation and surface passivation. For GaAs, InP, and GaP nanocrystals, spherical geometries of the desired size were cut from the corresponding bulk lattices and relaxed using the conjugate gradient algorithm implemented in LAMMPS together with a previously parameterized Tersoff-type force field for III-V semiconductor materials. [187] The relaxed nanocrystal surfaces were then passivated with ligand pseudopotentials. [158] Representative zinc blende GaAs nanocrystal structures of different sizes are shown in Fig. 3.1, and the GaAs and InP nanocrystal configurations used in this work are given in Table 3.1.

Table 3.1: Sizes and configurations of the GaAs and InP nanocrystals used in the theoretical calculations.

Material	Diameter (nm)	Configuration
GaAs	2.8	Ga ₂₄₉ As ₂₆₄
GaAs	3.7	Ga ₅₅₅ As ₅₅₆
GaAs	4.1	Ga ₈₅₁ As ₇₉₆
GaAs	4.7	Ga ₁₁₈₁ As ₁₁₆₀
GaAs	5.5	Ga ₁₉₁₃ As ₁₈₉₆
GaAs	6.0	Ga ₂₄₆₃ As ₂₄₆₀
GaAs	6.6	Ga ₃₁₀₃ As ₃₁₂₀
GaAs	8.0	Ga ₅₈₀₇ As ₅₇₈₀
InP	2.3	In ₁₄₁ P ₁₅₂
InP	2.9	In ₂₄₉ P ₂₆₄
InP	3.6	In ₅₅₅ P ₅₄₄
InP	4.0	In ₇₂₇ P ₇₆₀
InP	4.8	In ₁₂₀₅ P ₁₂₀₈
InP	6.1	In ₂₄₆₃ P ₂₄₆₀

Given these relaxed atomistic structures, we constructed the quasiparticle Hamiltonian using the atomistic DeepPseudopot in the non-interacting electron picture on a real-space

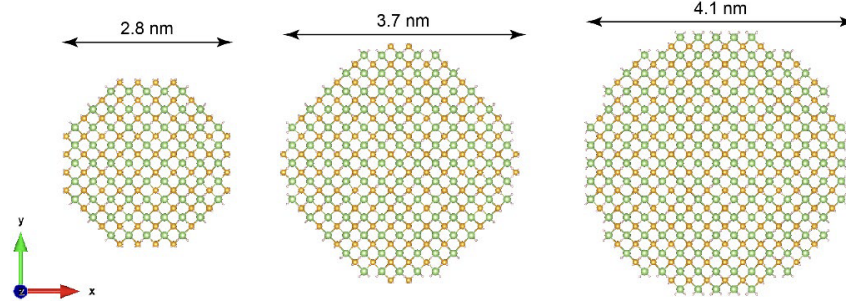


Figure 3.1: Configurations of 2.8nm, 3.7nm and 4.1nm diameter spherical GaAs nanocrystals used for atomistic theoretical calculations. The pseudo-ligands used for surface passivation in the calculations are replaced with H atoms. Atom colors: Ga – green, As – orange, H – white.

grid as in Eq. 3.1. We adopted newly fitted DeepPseudopot pseudopotentials for In, Ga, As, and P, trained to reproduce many-body perturbation theory (DFT+GW) reference quasiparticle band structures.

$$H_{qp} = -\frac{1}{2}\nabla^2 + \sum_{\alpha} v_{\alpha}(|\mathbf{r} - \mathbf{R}_{\alpha}|), \quad (3.1)$$

The nanocrystal Hamiltonians were then represented on a finely spaced real-space spinor grid basis with a grid spacing of 0.5 Bohr, which ensured accurate treatment of both the nonlocal pseudopotential components and the spin-orbit interaction through the projector formalism, as well as convergence of the single-particle eigenvalues near the band edges. This real-space representation is especially convenient for alloyed nanocrystals, as it naturally incorporates finite size, shape anisotropy, alloy disorder, and surface structure without requiring translational symmetry.

The nanocrystal Hamiltonians yields many eigenstates, yet only a relatively small subset of quasiparticle states near the semiconductor band edges is relevant to optical excitations. To obtain these states efficiently, we employed the stochastic filter diagonalization method, [188] which targets eigenstates within a chosen energy window and avoids the cost of full diagonalization while giving converged eigenenergies. The resulting quasiparticle states form the basis for the subsequent excitonic calculations.

Correlated electron-hole excitations were then obtained by solving the Bethe-Salpeter equation (BSE) within the static screening approximation, using the calculated quasiparticle states as the electron-hole product basis (Eq. 3.2) and assuming a single excitation description.

$$\psi_n(\mathbf{r}_e, \mathbf{r}_h) = \sum_{a,i} c_{a,i}^n \phi_a(\mathbf{r}_e) \phi_i(\mathbf{r}_h), \quad (3.2)$$

where a and i are electron and hole state indices, respectively. All the BSE calculations were converged to 0.001 eV of the exciton energy with the linear combination of 60 electron states

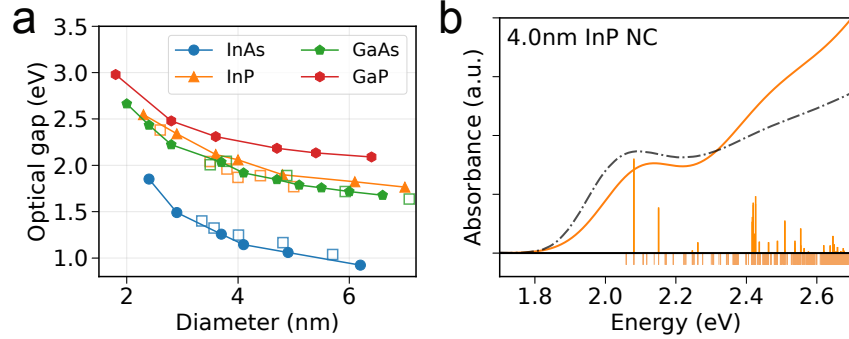


Figure 3.2: Optoelectronic properties of group III-V NCs calculated using the trained DeepPseudopot model. (a) Size-dependent optical gaps of InAs, InP, GaAs, and GaP NCs compared with experiments (hollow squares). [80, 190–192] (b) Calculated (orange solid line) and experimental (black dash-dot) absorption spectra for a 4.0 nm InP NC. Exciton energies (bars below axis) and oscillator strengths (bars above axis) are shown.

and 100–200 hole states, depending on the size of the nanocrystal. Size-dependent dielectric constants required for the BSE calculations were estimated from bulk values using the generalized Penn model. [189] The dielectric constants for the GaAs nanocrystals were chosen to be size-dependent, ranging from 9.39 (2.8 nm) to 11.25 (8.0 nm). For InP nanocrystals, the dielectric constants were chosen to range from 10.71 (2.3 nm) to 12.15 (6.1 nm). This step is essential because dielectric screening in confined nanocrystals differs substantially from the bulk limit and directly affects exciton binding energies and optical gaps.

The resulting calculated optical gaps reproduce the expected quantum-confinement trends across the binary III-V nanocrystal family. As shown in Fig. 1.2F and Fig. 3.2a, the optical gaps increase systematically with decreasing nanocrystal size for InAs, InP, GaAs, and GaP, while preserving the ordering inherited from the bulk materials with InAs having the smallest gaps and GaP the largest. The agreement with experiment is quantitative, with mean absolute errors of 0.057 eV for InAs, 0.113 eV for InP, and 0.046 eV for GaAs nanocrystals over the range of sizes considered. [80, 190–192] These results show that the DeepPseudopot-BSE framework captures both the absolute scale and the size dependence of the optical gaps across distinct III-V materials, providing a reliable atomistic description of excitonic quantum confinement.

For GaAs in particular, this agreement is especially significant. In bulk, GaAs is a direct-gap semiconductor with a room-temperature band gap of 1.42 eV and a large exciton Bohr radius of 11.6 nm. The colloidal GaAs nanocrystals studied here are therefore deep in the quantum-confined regime, and one expects their optical properties to vary strongly with size, much like the more established colloidal QD systems such as CdSe and InP.

Experimentally, this trend is evident already at the level of the sample appearance. The nanocrystal colloids evolve from orange for the smallest crystallites to nearly black for the largest ones (see Fig. 3.3), reflecting a pronounced size-dependent shift of the absorption onset. More importantly, the crude samples display diffuse but distinct excitonic features in the absorption spectrum (Fig. 3.3), demonstrating that the molten-salt synthesis yields GaAs nanocrystals of sufficiently high crystalline quality to support band-edge quantum-confined excitations. Within this context, the excellent agreement between the calculated optical gaps and the measured PL peak energies strongly supports the assignment of the observed emission to band-edge excitons rather than defect-related states. As the GaAs nanocrystal size increases, the optical gap decreases as expected from quantum confinement and, for sufficiently large nanocrystals, extends into the near-infrared while asymptotically approaching the bulk limit. Compared with CdSe and InP, GaAs nanocrystals exhibit smaller optical gaps at sizes above roughly 5 nm, consistent with the underlying differences in bulk band gaps, effective masses, and exciton Bohr radii. This combination of direct-gap character and broad size tunability makes GaAs nanocrystals particularly attractive as a new colloidal platform for tunable optoelectronic applications.

The optical activity of each excitonic transition was quantified through its oscillator strength, computed from the transition dipole moments between the ground state and the excitonic states.

$$f = \frac{4m_e E}{3\hbar^2 e^2} |\mu|^2, \quad (3.3)$$

where $\mu = e \sum_{a,i} c_{a,i}^n \langle \phi_a | \mathbf{r} | \phi_i \rangle$ is the transition dipole moment calculated using the quasiparticle wavefunctions and the BSE coefficients. E is the exciton energy. The oscillator strengths are directly connected to the intensity of absorption for the specific excitonic transition and the radiative lifetime. Radiative lifetimes at room temperature are calculated from the exciton energy and transition dipole moment for the calculated exciton states according to Eqns. 3.4 and 3.5,

$$\tau_r = \frac{3\pi\epsilon_0 \hbar c^3}{\omega^3 |\mu|^2}, \quad (3.4)$$

$$\tau_r^{tot} = \frac{1}{\frac{1}{Z} \sum_n \frac{e^{-\beta(E_n - E_0)}}{\tau_r^n}}, \quad (3.5)$$

where c is the speed of light, and $\hbar\omega$ is the exciton energy.

Using the exciton energies and oscillator strengths, the absorption spectrum was calculated as

$$I_{abs}(\hbar\omega) = \sum_n f_n \delta(\hbar\omega - E_n), \quad (3.6)$$

where E_n and f_n are the energy and oscillator strength for exciton n . The delta functions were approximated as Gaussian functions with standard deviation reflecting the inhomogeneity arising from size dispersion.

$$\delta(\hbar\omega - E) = \frac{1}{\sqrt{2\pi}\Gamma} \exp \left[-\frac{(\hbar\omega - E)^2}{2\Gamma^2} \right]. \quad (3.7)$$

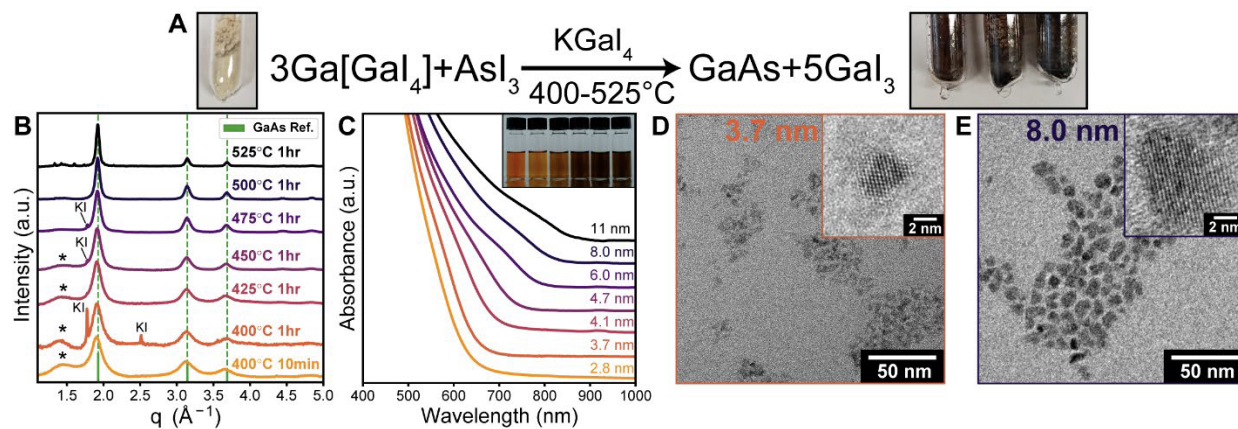


Figure 3.3: Direct synthesis of GaAs nanocrystals using Lewis neutral molten salt solvents. (A) Scheme of the reaction with photos of the ground salt precursor before (left) and after annealing at elevated temperatures (right), showing the black GaAs nanocrystals dispersed in the solidified salt matrix. The (*) peak originates from x-ray scattering from the organic ligand shell. We occasionally observe KI impurities which were not perfectly removed when separating the colloidal GaAs from insoluble precursors. (B) Powder x-ray diffraction patterns of GaAs nanocrystals synthesized using Lewis neutral molten salts. (C) UV-vis absorption spectra of colloidal GaAs nanocrystals synthesized at the reaction conditions in B. Inset are photos of the colloidal solutions of GaAs nanocrystals, showing distinct color changes as the size increases left (2.8 nm) to right (8 nm). Also shown are TEM and (inset) HRTEM images of GaAs nanocrystals synthesized at (D) 400°C for 1 hour and (E) 500°C for 1 hour.

This construction makes it possible to compare the discrete excitonic spectrum from theory directly to measured ensemble absorption spectra.

Theoretically calculated exciton fine structure, oscillator strengths and absorption spectra are shown in Fig. 3.2 for a representative example of a 4.0 nm InP QD, and in Fig. 3.4 for GaAs QDs ranging from 2.0 nm to 6.0 nm. The individual exciton energies are shown as sticks below the axis and their oscillator strengths as sticks above the axis, while the broadened theoretical absorption spectrum is compared directly to experiment (see also Fig. 3.3). For InP, the calculation reproduces both the first absorption peak position and the overall spectral envelope with good fidelity. For GaAs, the calculated absorption spectra are more structured than experimental measurements due to the size distribution in the experimental samples. Using a larger Gaussian broadening will yield similar spectral curves, but hide the detailed exciton level structure crucial for understanding the optical properties of GaAs QDs. This comparison is useful because it shows how the experimentally observed absorption features emerge from a sparse set of bright excitonic transitions whose energies and intensities are both determined by the atomistic electronic structure.

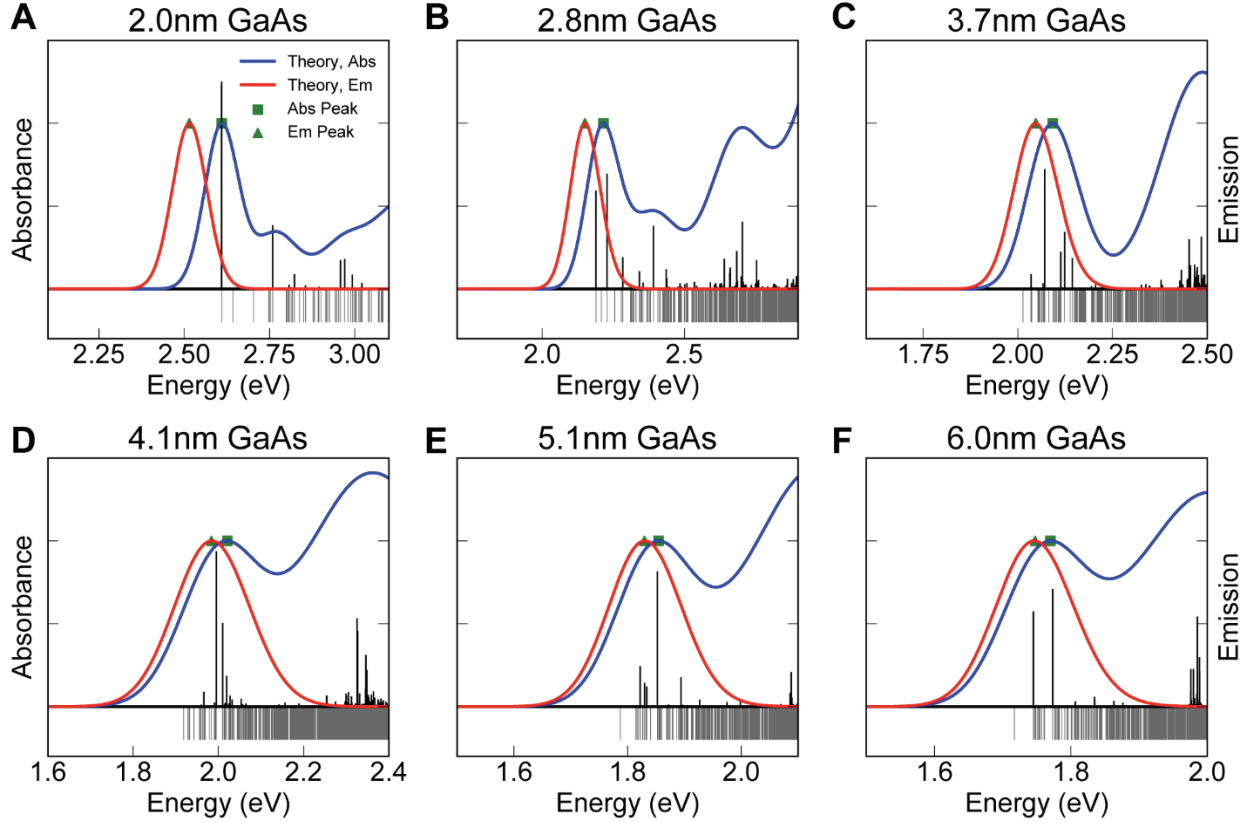


Figure 3.4: Calculated absorption (blue) and emission spectra (red) for GaAs nanocrystals of 2.0 nm to 6.0 nm diameter. The first peaks of the absorption spectra and the emission peaks are indicated by the green square and triangle, respectively. The exciton densities of states and oscillator strengths from theoretical predictions are plotted as gray sticks below the x-axis and black sticks above the x-axis, respectively.

To connect these electronic excitations to structural relaxation and spectral lineshapes, we further computed first-order exciton-phonon coupling from numerical differentiation of the real-space pseudopotentials. [193] In practice, the exciton-phonon Hamiltonian was expanded to lowest order in the phonon mode coordinates, and the coupling matrix elements were obtained by transforming the exciton-atomic-coordinate couplings into the phonon normal-mode basis (see Eq. 3.8). The latter was constructed from the mass-weighted Hessian matrix obtained from second derivatives of the Tersoff force field. This procedure yields mode-resolved couplings for each excitonic state and provides a microscopic description of how lattice motion perturbs the exciton manifold. Physically, these couplings quantify the displacement between the ground- and excited-state potential energy surfaces as a function

of lattice relaxation after vertical excitation.

$$V_{nm}^\alpha = \sum_{\alpha k} \frac{1}{\sqrt{m_\alpha}} \left[\sum_{abi} c_{ai}^n c_{bi}^m v'_{ab,\alpha} - \sum_{aij} c_{ai}^n c_{aj}^m v'_{ij,\alpha} \right], \quad (3.8)$$

where $v_{rs,\alpha} = \langle \phi_r | \frac{\partial v_\alpha(\mathbf{r}-\mathbf{R}_{\alpha k})}{\partial \mathbf{R}_{\alpha k}} | \phi_s \rangle$. ϕ_r and ϕ_s are the single-particle states, and $E_{\alpha k}$ is the eigenvector of the mass-weighted Hessian matrix. In Fig. 3.5, we show the exciton-phonon coupling results of a large GaAs NC. The phonon density of states is obtained from a classical force field. The spectral density is calculated using the DeepPseudopot model shows structured couplings primarily to a few acoustic phonon modes and strong coupling to discrete optical phonon modes, consistent with prior findings for other semiconductor NCs. [127, 194, 195]

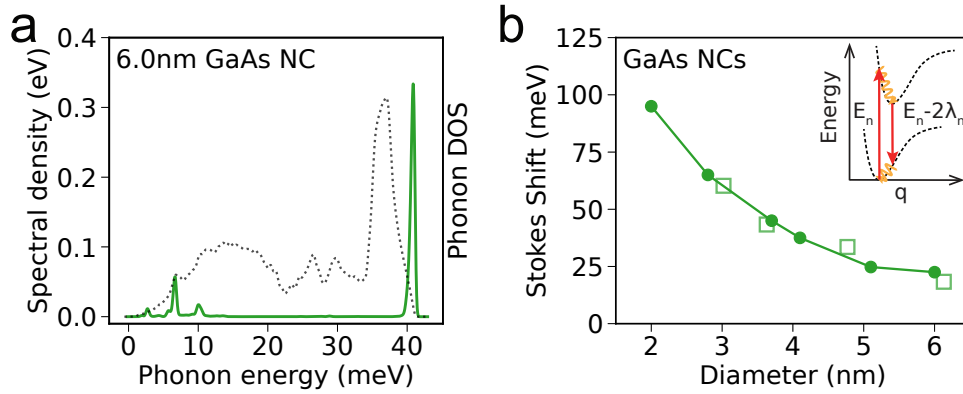


Figure 3.5: Electron-phonon coupling of group III-V NCs calculated using the trained DeepPseudopot model. (a) Exciton-phonon coupling spectral density (green) and phonon density of states (black dashed line) of a 6.0 nm GaAs NC. (b) Calculated (solid dots) and experimental (hollow squares) Stokes shifts for GaAs NCs as a function of size.

The phonon reorganization energy, sometimes also referred to as the lattice relaxation energy, measures the energetic stabilization associated with nuclear rearrangement after photoexcitation, and thus serves as a compact measure of exciton-phonon coupling strength. It is defined for the n -th exciton as in Eq. 3.9.

$$\lambda_n = \sum_{\nu}^{nPh} \frac{1}{2} \left(\frac{V_{nn}^{\nu}}{\omega_{\nu}} \right)^2. \quad (3.9)$$

The overall coupling strength of a nanocrystal can in turn be estimated by a Boltzmann thermal average over exciton states as $\lambda = \frac{1}{Z} \sum_n^{nExc} \exp(-\beta E_n) \lambda_n$. The calculated reorganization energies for GaAs, CdSe, and InP nanocrystals of different sizes show that GaAs

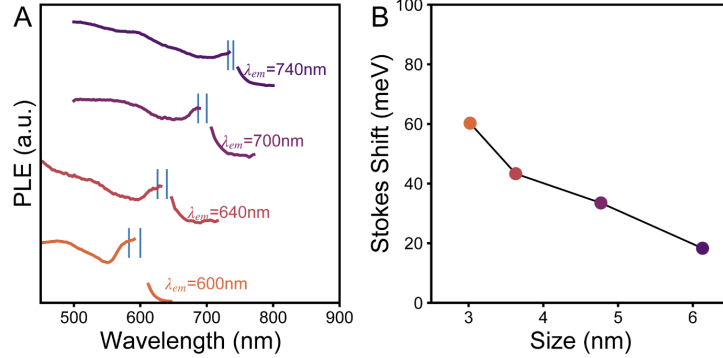


Figure 3.6: Experimental estimation of the Stokes shifts of GaAs nanocrystals. (A) PLE spectra collected with a detection wavelength 20 nm blue of the PL peak maximum for samples with different sizes. The blue lines represent the maximum of the PLE spectrum at the 1st exciton (left) and the detection wavelength (right). (B) Estimated Stokes shifts for GaAs nanocrystals as a function of size as determined by Scherrer analysis of XRD patterns. Samples are the same as presented in Fig. 3.

nanocrystals exhibit the smallest reorganization energies and therefore the weakest exciton-phonon coupling among the systems considered. This behavior reflects the relative rigidity of the Ga-As bond network, a feature that also underlies the strong performance of GaAs in bulk electronic and optoelectronic devices. Our calculations indicate that this same characteristic persists in the nanocrystal regime, with GaAs quantum dots displaying substantially weaker exciton-phonon coupling than CdSe and InP nanocrystals, consistent with the small Stokes shifts and related spectroscopic signatures observed experimentally.

The calculated exciton-phonon coupling also enable a direct simulation of experimentally measured Stokes shifts. The absorption and emission spectra were calculated from the exciton energies and oscillator strengths, with the emission spectrum additionally incorporating a thermal average over exciton populations. For each excitonic transition, the emission peak was redshifted relative to the vertical absorption energy by twice the corresponding reorganization energy, reflecting lattice relaxation in the excited state (see Eq. 3.6 and Eq. 3.10).

$$I_{em}(\hbar\omega) = \frac{1}{Z} \sum_n \exp(-\beta(E_n - E_0)) f_n \delta(\hbar\omega - (E_n - 2\lambda_n)). \quad (3.10)$$

In practice, the absorption and emission spectra were assembled by replacing the delta functions associated with discrete excitonic transitions by Gaussian functions whose widths reflect the inhomogeneity arising from size dispersion (see Eq. 3.7). The resulting absorption and emission spectra for GaAs nanocrystals spanning diameters from 2.0 to 6.0 nm are shown in Fig. 3.4. The atomistic DeepPseudopot-BSE framework, combined with exciton-phonon coupling and thermal broadening, provides a unified route from microscopic excited-state structure to the optical observables measured in ensemble spectroscopy.

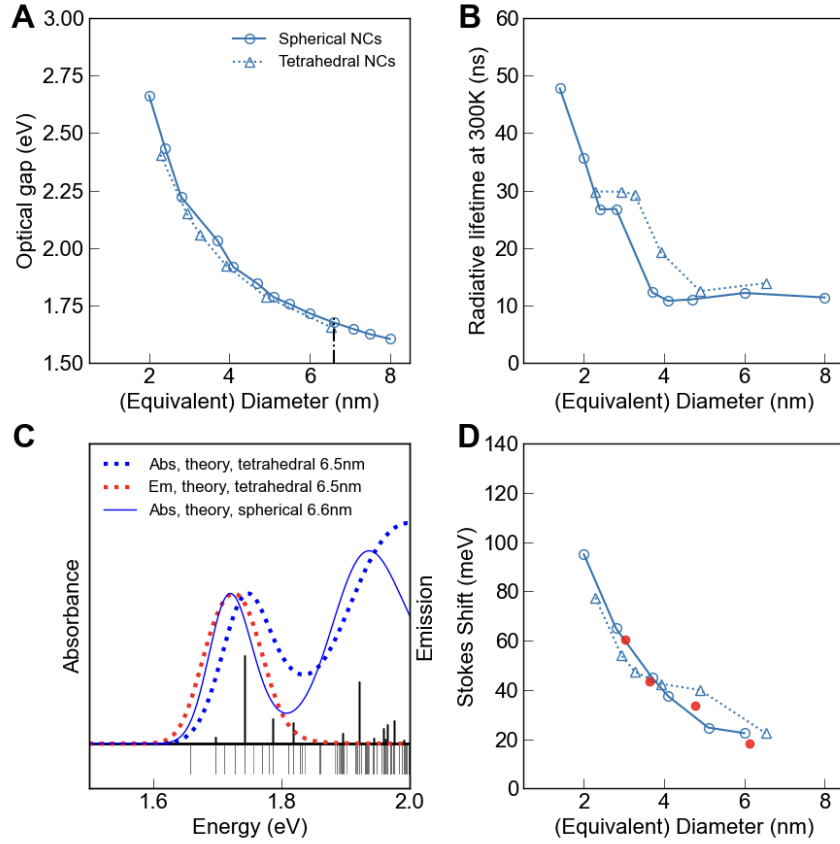


Figure 3.7: Comparison of optical properties between spherical (blue circles) and tetrahedral (blue triangles) GaAs nanocrystals, calculated using the atomistic semiempirical pseudopotential method: (A) the optical gap of the NCs, (B) the radiative lifetime at 300K, (C) the absorption and emission spectra of two NCs of similar diameters with different shapes, and (D) calculated Stokes shift compared to experimental measurements (red circles). The equivalent diameters of the tetrahedral nanocrystals are defined as the average of the diameters of the two spheres that inscribe and circumscribe the tetrahedron.

Experimentally, we observe a small shift between the absorption onset and the PL emission (see Fig. 3.6) suggesting there is a small Stokes shift. This suggests the PL is coming from a band edge state rather than a trap state. Further observation of sharp PLE spectra for different detection wavelengths across the PL spectrum indicates that the width of the PL spectrum is dictated by the size distribution of the sample and thus we are selecting different sub-populations with different detection wavelengths. Often in colloidal quantum dots where the emissive state is a shallow trap, size information is lost in the PLE spectra, with similar PLE spectra observed for different PL detection wavelengths, and the shape of

the PLE spectra approximately matches the absorption spectrum. We use PLE to estimate the size dependent Stokes shift from the GaAs quantum dots by measuring the energy difference between the 1st excitonic peak in the PLE spectrum and the detection wavelength, and we find Stokes shifts which vary from 60-20 meV as the size increases from 3 to 6 nm respectively. The size dependent Stokes shift follows well-established trends for other semiconductor quantum dots like CdSe. Altogether, the steady state optical characterization presented here suggests the GaAs nanocrystals are behaving like high quality semiconductor quantum dots and emitting from a band edge quantum confined state. In addition, the theoretically calculated Stokes shifts (Fig. 3.7D), calculated as the peak shift between the absorption and emission spectra, agree very well with the experimental measurements and further prove band edge emission and exciton fine structures of these GaAs nanocrystals.

In addition to spherical nanocrystals, tetrahedral GaAs nanocrystal geometries were constructed following the same procedure, starting from a regular tetrahedron cut from bulk zinc blende GaAs with cation-terminated surfaces. This allows the role of shape to be assessed within a common atomistic framework. The calculated optical gaps of the tetrahedral and spherical GaAs nanocrystals show the same quantum confinement trend (see Fig. 3.7) when the tetrahedron sizes were converted to the “equivalent” diameter, defined as the average of the diameters of the two spheres that respectively are inscribed in and circumscribed around the tetrahedron. In addition, similar Stokes shifts and radiative lifetimes were observed for NCs with the same confinement, regardless of shape. Exciton fine structures of the tetrahedral-shaped GaAs NCs, especially the exciton state degeneracy at the band edge, are different from the spherical counterparts, but such distinction is hard to detect experimentally via ensemble steady-state spectroscopy.

3.2 Simulating single-NC phonon-resolved PL spectroscopy

Introduction and motivation

The optical properties of colloidal semiconductor nanocrystals (NCs) have been extensively studied over the last several decades,[51, 59, 84, 196–199] leading to the development of novel optoelectronic devices.[200–205] Many studies have aimed to understand the photoluminescence (PL) line shapes and, in particular, the dominant channels and couplings governing the homogeneous contributions to the linewidth.[101, 104, 111, 199, 206–211] Particularly, low-temperature single-NC PL measurements have been commonly used to delineate the homogeneous contributions, indicating complex structures of sidebands resulting from the coupling of excitons to acoustic and optical phonons.[111, 195, 212–217] On the other hand, the exciton-phonon coupling parameters obtained in these low-temperature studies were not able to reconcile the broad, application-relevant, room-temperature emission linewidths, resulting in a lack of consensus on the strength and nature of exciton-phonon interactions in NCs. A thorough understanding of the structure of the NC PL spectrum and its temperature dependence calls for an atomistic, parameter-free theoretical approach that calculates the phonon-resolved PL line shapes of NCs. For smaller clusters, one can use first-principle methods, but these are limited by computational complexity.[120]

In this section, we demonstrate an atomistic theory development that accurately describes the exciton energies, phonon modes, and exciton-phonon couplings of NCs of experimentally relevant sizes.[108, 193] To test and validate this approach, we first compare the predictions from our theory with single-NC PL measurements for CdSe/CdS core-shell NCs across a wide range of temperatures, from 4 to 290 K, where common experimental challenges, such as photo-charging, bleaching, and thermal drift, were greatly reduced.[218] Then, we apply the methods to GaAs QDs and compare the predicted single-NC emission spectral features to experimental fluorescence line narrowing (FLN) and photoluminescence excitation (PLE) signatures. We analyze the spectral features across CdSe/CdS and GaAs QDs, pointing out universal features regarding nanocrystal sizes, core-shell configurations, and exciton-phonon coupling strengths, etc. Lastly, we briefly discuss how second-order exciton-phonon coupling can modify fine spectral structure and lineshape asymmetries, and outline how such effects can be incorporated in extended models.

Linear response model for lineshape

We start with a model Hamiltonian that describes the ground state, a manifold of excitonic states, a bath of phonons, and the exciton-phonon couplings (expanded to lowest order in

the phonon mode coordinates) for an NC,[193] weakly perturbed by an electromagnetic field:

$$\begin{aligned}
 H = & E_g |\psi_g\rangle \langle \psi_g| + \sum_n E_n |\psi_n\rangle \langle \psi_n| \\
 & + \sum_\alpha \hbar \omega_\alpha b_\alpha^\dagger b_\alpha + \sum_{\alpha n m} V_{n,m}^\alpha |\psi_n\rangle \langle \psi_m| q_\alpha \\
 & + \epsilon \sum_n \mu_{gn} \cos(\omega t) |\psi_g\rangle \langle \psi_n| + h.c. .
 \end{aligned} \tag{3.11}$$

Here, E_g , $|\psi_g\rangle$, E_n , and $|\psi_n\rangle$ are the energies and wavefunctions for the ground and n -th excitonic states, respectively, which are obtained using the atomistic semiempirical pseudopotential method [150, 158, 160] combined with the Bethe-Salpeter Equation (BSE).[135, 219] The exciton-phonon couplings, $V_{n,m}^\alpha$, between excitonic states $|\psi_m\rangle$ and $|\psi_n\rangle$ through phonon mode α were also calculated from the semiempirical pseudopotential model combined with the BSE.[193] In practice, we assume that population relaxation does not have a large effect on the overall dephasing time, and we only include the diagonal coupling elements, $V_{n,n}^\alpha$, since they dominate the spectral line shape. Finally, the external electromagnetic field with strength ϵ and frequency ω couples the ground state and the n -th excitonic state through the transition dipole μ_{gn} . The excitonic states are taken as the “system”, and all phonon modes are grouped into the “bath”.

The emission spectrum is given by the Fourier transform of the transition dipole auto-correlation function, obtained within linear response theory:[220]

$$\begin{aligned}
 I(\omega) &= \frac{1}{Q_n} \sum_n e^{-\beta E_n} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \hat{\mu}_H(t) \hat{\mu}_H(0) \rangle \\
 &= \frac{1}{Q_n} \sum_n e^{-\beta E_n} |\mu_{gn}|^2 \int_{-\infty}^{\infty} dt e^{-i(\omega - \omega_{ng})t} \langle F_n(t) \rangle ,
 \end{aligned} \tag{3.12}$$

where we assumed a thermal Boltzmann average over initial excitonic states. In the above equation, $Q_n = \sum_n e^{-\beta E_n}$ is the partition function of excitons and $\omega_{ng} = (E_n - E_g)/\hbar$.

Given the partitioning between the “system” (only the purely excitonic states) and the “bath” (all the phonon modes), the dephasing function, $\langle F_n(t) \rangle$, contributes not only to the width of each spectral feature but to the existence of well-resolved phonon sidebands. It can be calculated using a cumulant expansion to second order provided the bath modes are harmonic,[221] and is given by the following exact expression for the model Hamiltonian (c.f., Eq. (3.11)).

$$\langle F_n(t) \rangle = \exp \left\{ \frac{1}{2\hbar} \sum_\alpha \frac{(V_{n,n}^\alpha)^2}{(\omega_\alpha)^3} [C_\alpha^\Re(t) + iC_\alpha^\Im(t)] \right\}, \tag{3.13}$$

where $C_\alpha^\Re(t) = \coth(\beta\hbar\omega_\alpha/2)(\cos\omega_\alpha t - 1)$ and $C_\alpha^\Im(t) = \sin\omega_\alpha t - \omega_\alpha t$. The use of the dephasing function for simulation of linear spectroscopy has been widely applied to molecular as well as condensed phase systems.[222–224] The full quantum mechanical formulation of the dephasing functions (Eq. 3.13) for when the system-bath (i.e., exciton-phonon) coupling is linear in the normal mode coordinates has been derived by many earlier works.[221, 225–227]

The anharmonicity of atomic motion at high temperatures and its relations with the width and shape of the PL spectrum is also analyzed. We concluded that the finite lifetimes of phonons only broadens the FWHM of PL spectra by around 10meV at 300K, and is thus insufficient to explain the mismatch in FWHM - temperature relationship between our linear exciton-phonon coupling model and the experimental single-NC measurements. We then empirically correct the dephasing rate by accounting for higher-order expansion terms in the exciton-phonon couplings, and analyze these additional decay channels (as discussed in the main text). Here, the details of anharmonicity are given.

The finite lifetime of the phonons were calculated following the methods outlined in Ref. [228]. The relaxation lifetimes $1/T_1$ of each phonon mode in a 3.0 nm core, 3ML shell CdSe/CdS nanocrystal were calculated from the velocity auto-correlation function $C(t) = \langle v(0)v(t) \rangle$ using the following relation:[228]

$$\frac{1}{T_1} = \tilde{\xi}'(\omega) = \Re \left[\frac{C(0) - i\omega \tilde{C}(\omega)}{\tilde{C}(\omega)} + i\omega \right], \quad (3.14)$$

where $\tilde{\xi}'(\omega)$ is the real part of the Laplace transform of the friction kernel from the generalized Langevin equation at the frequency of the mode. The velocity auto-correlation functions were calculated directly by simulating molecular dynamics (MD) trajectories which were sampled from a microcanonical ensemble at 300K. The same Stillinger-Weber force field parameterized for bulk CdSe and CdS (as described in the main text and earlier sections of the SI) was used. The transformation from atomic coordinates to phonon mode coordinates was done through the eigenvectors of the mass-weighted Hessian matrix. The lifetimes of phonons that couple most strongly to the ground bright excitonic state have the most significant effects on the dephasing dynamics. The MD simulations reveal that the most strongly coupled acoustic phonons at ~ 0.5 THz have lifetimes of about 1 ps, while the CdSe optical phonon modes at ~ 8 THz have lifetimes of around 100 fs.

The finite phonon lifetime is incorporated into the bath correlation function by considering its damping effect on each phonon motion. The equations of motion of the creation and annihilation operators in these quantum mechanical, damped harmonic oscillators can be rewritten as:

$$\dot{\hat{b}}_\alpha = -i\omega_\alpha \hat{b}_\alpha - \frac{1}{T_1} \hat{b}_\alpha, \quad h.c., \quad (3.15)$$

where $\hat{b}_\alpha$ and $\hat{b}_\alpha^\dagger$ are the annihilation and creation operators for phonon mode α with frequency ω_α and lifetime T_1 . For simplicity, we assume that all phonons have the same lifetime and thus, the bath correlation function for the damped harmonic oscillator is exponentially damped.

$$\langle q_\alpha(t) q_\beta(0) \rangle = e^{-\frac{t}{T_1}} \langle q_\alpha(t) q_\beta(0) \rangle_{HO}, \quad (3.16)$$

From here, we can plug in the damped bath correlation to obtain the analytical PL spectra:

$$I(\omega) = \frac{1}{Q_n} \sum_n e^{-\beta E_n} |\mu_{gn}|^2 \int_{-\infty}^{\infty} dt e^{i(\omega - \omega_{ng})t} \exp \left\{ \frac{1}{2\hbar} \sum_\alpha \frac{(V_{n,n}^\alpha)^2}{(\omega_\alpha)^3} C_\alpha^{DHO}(t) \right\}, \quad (3.17)$$

where for the each damped harmonic oscillators,

$$C_{\alpha}^{DHO}(t) = \omega_{\alpha}^2 \cdot \left[(n(\omega_{\alpha}) + 1) \frac{e^{-t/T_1 - i\omega_{\alpha}t} + \frac{t}{T_1} + i\omega_{\alpha}t - 1}{(\frac{1}{T_1} + i\omega_{\alpha})^2} + n(\omega_{\alpha}) \frac{e^{-t/T_1 + i\omega_{\alpha}t} + \frac{t}{T_1} - i\omega_{\alpha}t - 1}{(\frac{1}{T_1} - i\omega_{\alpha})^2} \right], \quad (3.18)$$

Using the phonon lifetime $T_1 \approx 100$ fs at 300K for 3nm CdSe / 3ML CdS core-shell nanocrystal, we obtained the anharmonic correction to the PL spectrum. At 300K, incorporating anharmonicity increases the model PL FWHM from 28.2meV (for harmonic phonons) to 37.8meV. This correction of ≈ 10 meV in the single-NC FWHM only accounts for a very small fraction of the discrepancy between the experimental linewidth (68.10meV) and our model with linear exciton-phonon coupling(28.2meV). Thus, we ruled out anharmonicity as the primary mechanism for the temperature-activated emission channel, and investigated high-order exciton-phonon coupling expansions, as discussed in the main text.

Photoluminescence lineshape of CdSe/CdS nanocrystals

The configurations of the core-shell CdSe/CdS NCs in theoretical calculations were constructed by first cutting the desired core size from bulk wurtzite CdSe geometry, and then adding several monolayers of shell (CdS). The core-shell geometries were relaxed using the conjugate gradient minimization with the classical Stillinger-Weber force field, which was previously parameterized for the bulk CdSe and CdS systems.[229] Upon geometry relaxation, the outermost layer of atoms were removed and replaced with ligand pseudopotentials representing the passivation layer.[108, 160] The molecular formulae, core diameters, shell thicknesses, overall diameters and geometries are summarized below in Table 3.2 for all the CdSe/CdS core-shell NCs calculated in this work.

Configuration	Core diameter (nm)	Shell thickness (ML)	Overall diameter (nm)
Cd ₇₅₃ Se ₂₅₂ S ₅₀₁	3.0	2	4.6
Cd ₁₁₉₇ Se ₂₅₂ S ₉₄₅	3.0	3	5.4
Cd ₁₇₈₈ Se ₂₅₂ S ₁₅₃₆	3.0	4	6.2
Cd ₂₅₄₇ Se ₂₅₂ S ₂₂₉₅	3.0	5	7.0
Cd ₁₁₉₇ Se ₄₈₃ S ₇₁₄	3.9	2	5.4
Cd ₁₇₈₈ Se ₄₈₃ S ₁₃₀₅	3.9	3	6.2
Cd ₂₅₄₇ Se ₄₈₃ S ₂₀₆₄	3.9	4	7.1
Cd ₃₄₉₅ Se ₄₈₃ S ₃₀₁₂	3.9	5	7.9

Table 3.2: CdSe/CdS core-shell NC geometry details.

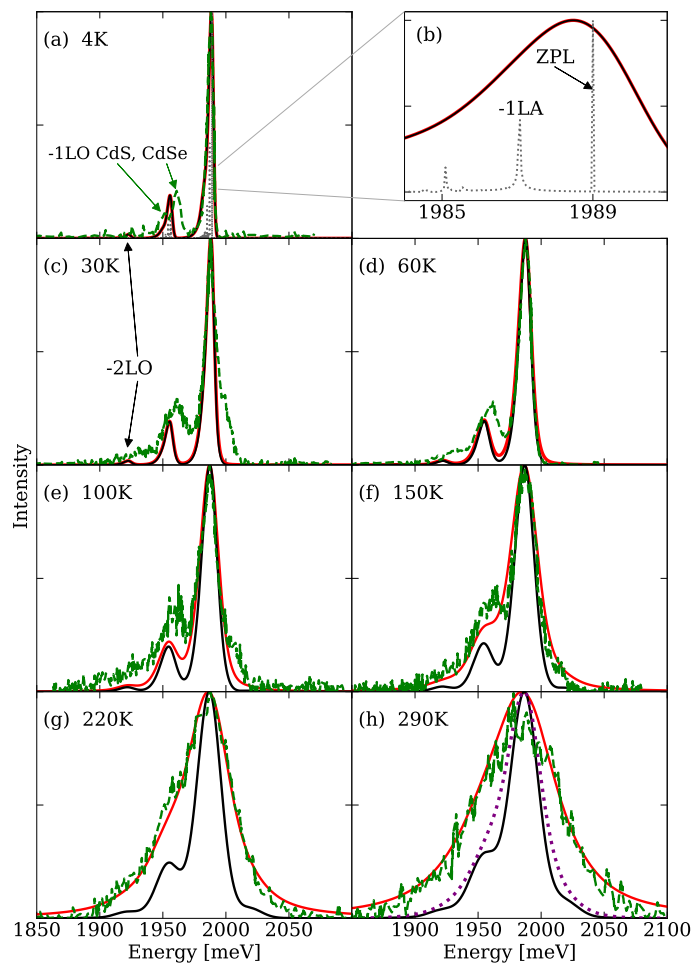


Figure 3.8: Single-molecule photoluminescence spectra for a 3nm diameter CdSe / 3ML CdS core-shell NC at temperatures ranging from 4 to 290 K. The calculated results from the model Hamiltonian (black curves) and from the empirical inclusion of second-order expansion of exciton-phonon couplings (red curves) are compared to the experimental measurements (green dashed lines). (a) The theoretical model results before (dotted line) and after broadening (black solid line) at 4K are shown. Longitudinal optical phonon sidebands (-1LO) corresponding to CdSe and CdS, and phonon satellite overtones (-2LO) are distinguished. (b) A zoomed-in view around the zero-phonon line (ZPL) is shown, identifying several longitudinal acoustic phonon sidebands (-1LA). (c) - (g) The calculated and measured PL spectra at 30, 60, 100, 150, and 220K are shown. (h) At 290K, the calculated spectrum that accounts for the anharmonicity of atomic motion via the finite phonon lifetime is also shown (purple curve).

In Fig. 3.8, we plot the PL spectra of a wurtzite 3nm CdSe core / 3 monolayer (ML) CdS shell NC for different temperatures and compare the temperature-dependent single NC measurements of the same NC (green dashed curves) to predictions from our model (solid black curves). In comparing the experimental results with our theoretical predictions, we shifted the onset of emission due to small differences in the optical gaps ($\sim 130\text{meV}$) resulting from an additional 1-2 ML of ZnS coating in the experiments. Additionally, to compare our simulated results with experiments, we assume a Gaussian broadening of 4meV , which accounts for experimental broadening due to the spectrometer spectral resolution and spectral diffusion. The emission shift and Gaussian broadening are the only empirical parameters used to calculate the line shapes (solid black curves) from Eqs. (3.12) and (3.13).

We also analyzed whether surface irregularities and various geometries of NCs changes the PL spectra and its spectral features at low temperatures. We conducted additional calculations on 1) a $3.0\text{nm}/3\text{ML}$ CdSe/CdS NC with an irregular faceted surface and 2) a similarly sized CdSe/CdS NC with a less-faceted, spherical surface. As shown in Fig. 3.9A, the geometry of the less-faceted NC was created by cutting a sphere from a larger core-shell NC, and irregular surfaced NC was created by removing one Cd and one S atom from the regular NC edges to create “ruggedness” in the surface. The resulting spectral densities and the low-temperature (4 K) PL spectra are plotted in Fig. 3.9B and C. Compared to the regular CdSe/CdS NC, the two NCs with less faceted (blue curve) or less regular surface (red curve) gives nearly the same spectral density and exactly the same PL spectral line shape, with the same ZPL linewidth and LO phonon sidebands. We note that although the surface ruggedness was created by only removing 2 atoms, it is representative of other surface irregularities existent in experimental NCs.

And thus, with these two additional calculations, we confidently conclude that the model, analysis and conclusions of PL line shape in the current work aren’t susceptible to NC geometry irregularities. The structures in the PL spectrum at 4 K and the sparse spectral density in our calculations aren’t artifacts of the symmetric NC geometry. The use of a faceted and symmetric NC structure for calculation is safe and justified.

The experimental spectrum at low temperatures consists of a slightly asymmetric narrow center peak and distinct phonon sidebands, which is consistent with earlier studies.[101, 194, 195, 211, 212, 218] As the temperature increases, the line shape evolves into a broader structure, and at the crossover temperature $T_c \approx 200\text{K}$, it turns into a featureless, broad peak. Our theoretical model shows good agreement with the single-NC PL measurements at low and intermediate temperatures ($T \leq T_c$), providing a quantitatively accurate description of the relative positions and intensities of the zero-phonon line (ZPL) and the phonon sidebands, as well as their temperature dependence. As temperature increases above T_c , we observe small deviations between the predicted and measured spectra, which become more significant at higher temperatures, suggesting that there is an additional emission channel that is not included in our model Hamiltonian, as discussed further below. One such source for additional broadening is higher-order terms (beyond linear) in the expansions of the exciton-phonon couplings (Duschinsky rotations). The red curves in Fig. 3.8 include an empirical correction that accounts for the contributions of higher-order couplings at tem-

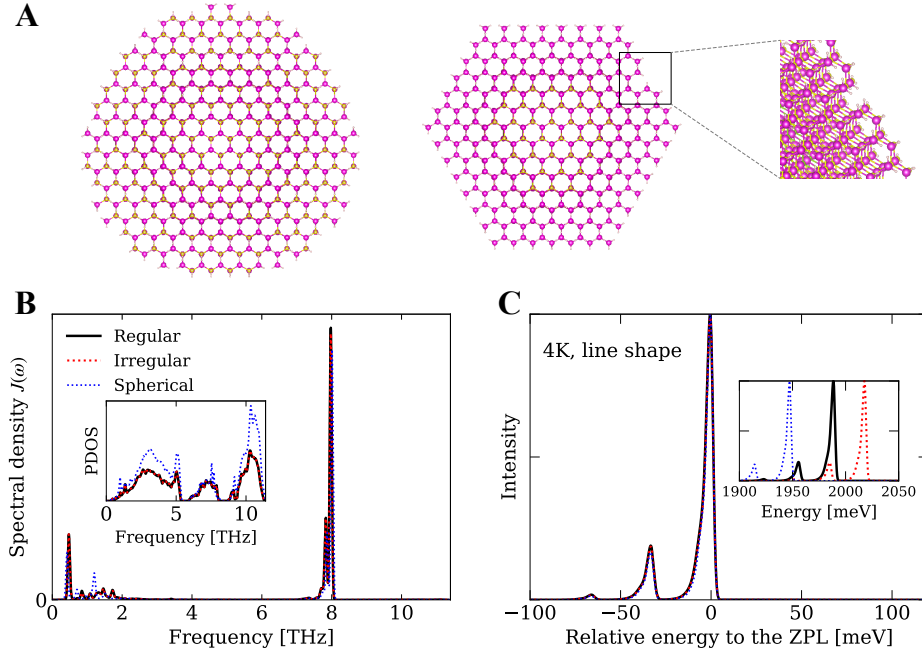


Figure 3.9: (A) The geometries of a less-faceted (left) and an irregularly surfaced (right) 3.0nm CdSe/3ML CdS core-shell NC are shown. The area with rugged CdS finish is zoomed in for a more detailed view. (B) The calculated phonon spectral densities and phonon densities of states (PDOS, inset) of the less-faceted, spherical NC (blue dotted lines) and irregular surfaced NC (red dotted lines) are compared to those of the regular-surface core-shell NC (black solid lines). (C) The PL spectral line shapes at 4 K are compared for the core-shell NC with regular surface (black solid line), irregular surface (red dotted line), and spherical surface (blue dotted line). The spectra are shifted such that the zero-phonon line (ZPL) is at 0. In the inset, the spectra without the energy shifts are shown for reference.

peratures above T_c , resulting in excellent agreement with the experimental measurements across all temperatures. The crossover temperature is expressed in our model by equating the dephasing rate contributions from linear-order and from higher-order exciton-phonon couplings.

In the limit that $T \rightarrow 0\text{K}$, the calculated zero-phonon line becomes infinitely narrow with transition energies corresponding to the excitonic (optical) gap,[221, 230] as shown in Fig. 3.8(b). In addition, we observe several longitudinal *acoustic* (LA) phonon sidebands that merge with the broadened ZPL to form one main peak with a slight asymmetry that matches experiments. Acoustic phonon modes are the collective coherent movement of atoms in the lattice, as opposed to optical phonons which are out-of-phase movements of the atoms in the lattice. Moreover, only emissions from spin-allowed (bright) excitons are considered

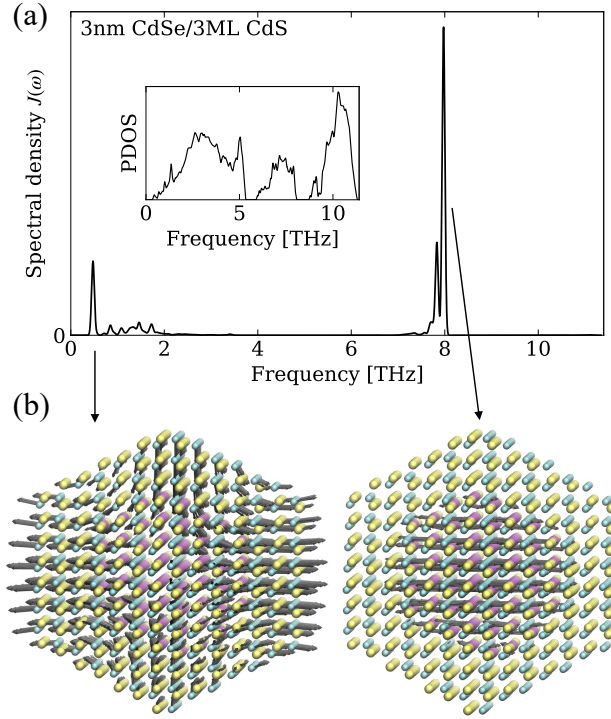


Figure 3.10: (a) The calculated spectral density of a 3nm core, 3ML shell CdSe/CdS NC using our model. The inset shows the phonon density of states for this core-shell NC. (b) The motions of one acoustic phonon mode and one optical phonon with the strongest coupling to the exciton are shown. Color schemes: blue-Cd, purple-Se, yellow-S, black arrows-phonon mode motion.

in our model. This is motivated by the fact that in NCs of similar sizes, the bright-dark exciton energy splitting is on the scale of $\sim 2\text{meV}$, [215, 231–234] smaller than the resolution of experimental measurements in this work. In addition, calculated phonon emission line shapes at $T = 4\text{K}$ from spin-forbidden (dark) excitons are similar to those from the bright excitons, and therefore, the analysis of exciton-phonon couplings remains the same (see the SI for more information). Our model also identifies some of the *optical* phonon sidebands, particularly those associated with the longitudinal optical (LO) phonon frequency of CdSe (6.29 THz), that remain distinct from the ZPL even at elevated temperatures ($T \leq T_c$). Moreover, due to phonon emission, -2LO phonon satellite overtones are visible at energies lower than the optical transition in both the experimental and modeled spectra. The position of the CdSe LO phonon sideband is slightly shifted compared to the experiments, mainly due to inaccuracies of the classical Stillinger-Weber force field, which was parameterized for bulk semiconductors. Our model's prediction of the phonon sideband position can be systematically improved as better force fields are developed. In addition, the CdS LO phonon

sideband observed experimentally at low temperatures (which otherwise merges with the CdSe LO phonon sideband) is absent in the calculated spectra. In our model, the very small coupling to the CdS LO phonons can be explained by the core-localization of the exciton hole states given the quasi-type II band alignment of CdSe/CdS core/shell NCs. As demonstrated in earlier works, the magnitude of the hole channel phonon coupling is significantly larger than the electron channel.[193, 235] And thus, the overall exciton coupling to the shell (CdS) LO phonons is very small. Furthermore, we cannot exclude emission from the charged trion state experimentally, which is known to be emissive in thick-shell CdSe/CdS, and for which we expect higher coupling to shell LO modes.

To further analyze the contribution of the individual phonon modes to the spectra, we define the spectral density, which measures the strength of couplings between the exciton and the phonon modes:

$$J(\omega) = \sum_{\alpha} \left(\frac{V_{n,n}^{\alpha}}{\omega_{\alpha}} \right)^2 \delta(\omega - \omega_{\alpha}) . \quad (3.19)$$

The spectral density is plotted in Fig. 3.10(a) for a 3nm CdSe / 3ML CdS NC. Fig. 3.10(b) shows an acoustic mode and an optical mode with the strongest coupling to the lowest bright exciton. The motions along the optical mode are primarily restricted to the CdSe core as a result of the localization of the hole to the CdSe core, while the motion along the breathing mode involves atoms in both the core and shell. Similar results were observed for other core sizes and shell thicknesses. The strong coupling to the optical phonons in the core-shell NC is consistent with earlier experimental [101, 211, 237, 238] and theoretical [109, 239–243] investigations.

In Fig. 3.11, we analyze the temperature dependence of the PL linewidth for single particle and ensemble measurements. Obtaining the FWHM from the analytical calculations of the spectra is tricky, since our model Hamiltonian lacks a dephasing time [221] and exhibits recurrences due to the finite number of phonon modes, resulting in infinitely narrow vibronic peaks. In order to reveal the intrinsic dynamics of the electronic transition and calculate experimentally-relevant FWHM, we convolved the calculated vibronic spectra with a time-domain Gaussian filter function with a width of $\sim 4\text{meV}$ before comparing with experimental single-molecule PL measurements. This width is also consistent with the instrument resolution limit of the experimental setup, and the timescale of the decay of this filter function is faster than the recurrence time, $t_r \approx 2\pi/\omega_{min}$. Furthermore, to match ensemble measurements, we convolved the calculated spectrum with another (broader) Gaussian function to account for the nearly-normal distribution of inhomogeneity of local environments in ensemble PL experiments. At very low temperatures ($k_B T < \hbar\omega_{min}$), the single particle measurements (green circles) of the full width at half maximum (FWHM) are bound by the experimental resolution ($\approx 5\text{meV}$) and increase monotonically as T increases, with a notable change in the slope at $T_c \approx 200\text{K}$, which we call the crossover temperature. The FWHM for the ensemble measurements from Ref. [236] (green squares) is significantly larger than the single particle measurements due to inhomogeneous broadening, with a similar change

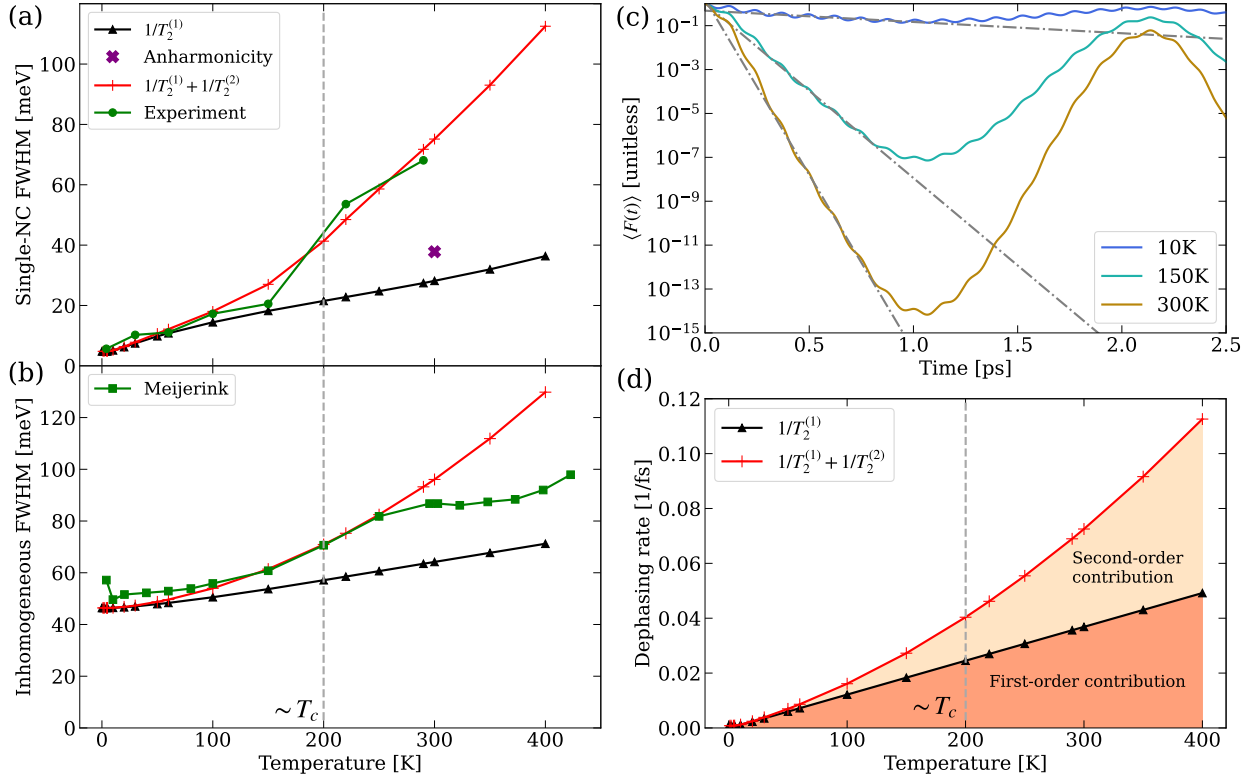


Figure 3.11: (a) The temperature dependence of PL linewidth of single-NC PL spectra on a 3nm/3ML CdSe/CdS NC. The linewidths calculated by the model (black triangles) are compared to experimental results (green circles). The linewidth at 300K calculated with anharmonicity of the atomic motion is shown as the purple cross. Dephasing contributions from second-order exciton-phonon couplings are included empirically in the red curve. (b) The temperature dependence of inhomogeneous PL linewidth in ensemble measurements on 3nm/2ML CdSe/CdS NCs. Experimental results are shown in green squares and adapted from Ref. [236]. The black and red curves show the model results following the same labeling conventions as in panel (a). (c) The dephasing function $\langle F(t) \rangle$ calculated analytically using Eq. (3.13) in a semi-log plot at three representative temperatures. The first-order dephasing rates (dash-dot lines) are extracted from the exponential-decay regime of the dephasing function before recurrences happen. (d) The dephasing rate contributions from first- and second-order exciton-phonon couplings at various temperatures (see Eq. (3.20)).

in the temperature dependence observed at T_c (see further discussion below for the physical interpretation of the crossover temperature).

At low and intermediate temperatures ($T \leq T_c$), the results obtained from the model Hamiltonian (black curves) show excellent agreement with the experimental measurements at both the single-particle (Fig. 3.11(a)) and ensemble levels (Fig. 3.11(b)). At temperatures

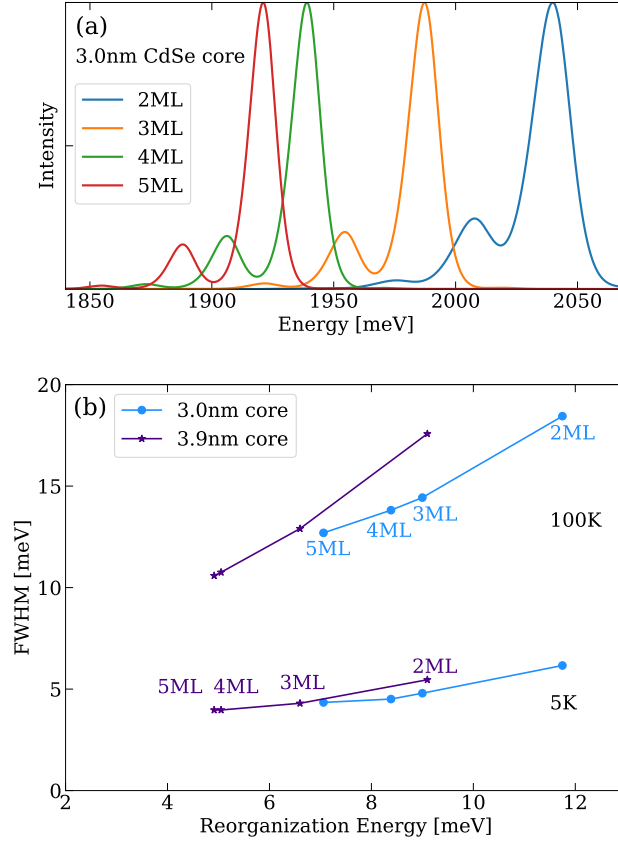


Figure 3.12: (a) Single-NC PL spectrum progression for a CdSe/CdS core-shell NC of 3 nm core diameter and various shell thicknesses at an intermediate temperature (100K). (b) The spectral linewidth vs. reorganization energy at 5 and 100K for NCs with 3 nm or 3.9 nm diameter CdSe cores and 2 to 5 monolayers (ML) of CdS shells. For all spectra calculations, a Gaussian broadening of 4meV is included to account for the spectrometer spectral resolution in the experiments.

above T_c , the calculated width (black curves) shows notable deviations from the measured linewidth (green curves), as indicated above. First, we studied the anharmonicity of the atomic motion as a possible source of such deviations by evaluating the finite lifetimes of phonons using classical molecular dynamics simulations [228] (see SI for more information). As shown in purple in Fig. 3.8(h) and Fig. 3.11(a), at 300K, incorporating finite phonon lifetimes into the spectrum resulted in an increase of only ≈ 10 meV in the single-NC FWHM, and therefore anharmonic motion is ruled out as the primary mechanism to explain the discrepancy between the experiments and theory. In addition, no temperature-activated spectral diffusion pathways have been identified,[213, 218, 244] suggesting that the role of spectral diffusion at high temperatures is similar to that at low temperatures, where the

contribution to the linewidth due to spectral diffusion is negligible.

The discrepancy at high temperatures between the experiments and theory can also result from higher-order expansion terms in the exciton-phonon couplings. These higher-order terms physically manifest as the difference in normal modes (frequency shifts and mode-mixing) between the ground and excited states, and they are separate from anharmonicity in the bath Hamiltonian. To account for these additional decay channels, we empirically correct the long-time decay rate of the dephasing function ($F(t) \propto \exp(-t/T_2)$) as follows:[221]

$$\frac{1}{T_2} = \frac{1}{T_2^{(1)}} + \frac{1}{T_2^{(2)}}, \quad (3.20)$$

where the dephasing rate due to the first-order coupling,

$$\frac{1}{T_2^{(1)}} = \pi \frac{\lambda}{\hbar} \frac{k_B T}{\hbar \omega_c}, \quad (3.21)$$

is extracted from the exponential-decay of the dephasing function (c.f., Eq. (3.13)), as shown in Fig. 3.11(c). In the above equation, the reorganization energy is defined as $\lambda = \frac{1}{2} \sum_{\alpha} \left(\frac{V_{n,n}^{\alpha}}{\omega_{\alpha}} \right)^2$, and ω_c is the characteristic frequency of the bath. Assuming that the second-order coupling terms dominate the contribution from higher-order terms, the temperature dependence can be approximated by Eq. (3.22) (See Ref. [221]).

$$\frac{1}{T_2^{(2)}} = W^2 \pi \int_0^{\infty} d\omega n(\omega) (n(\omega) + 1) \omega^2 J^2(\omega), \quad (3.22)$$

where W is the magnitude of second-order exciton-phonon coupling and is determined empirically. $n(\omega)$ is the Bose-Einstein distribution, and $J(\omega)$ is the spectral density defined in Eq. (3.19). In Fig. 3.11(d), we plot the total (red curve, Eq. 3.20) and first-order (black curve) dephasing rates as a function of temperatures. At low temperatures, the dephasing rate is governed by the first-order term, while as the temperature increases, the contributions of the first- and higher-order terms become comparable. The temperature dependence of the total dephasing rate explains the change in slope of the FWHM as temperature increases above T_c , as shown by the red curves in Fig. 3.11(a) and (b). At temperatures around $k_B T_c = 2/W^2 \lambda$, the first-order and second-order dephasing rates contribute equally, leading to a temperature-crossover behavior.

Upon validating our model Hamiltonian against single-NC and ensemble PL measurements below T_c , we applied the model to a series of CdSe/CdS core-shell nanocrystals of various core sizes and shell thicknesses at an intermediate temperature of 100K, at which distinct phonon sidebands are still visible, as shown in Fig. 3.12. The intermediate-temperature spectra are calculated with a Gaussian broadening of 4meV that accounts for the spectrometer spectral resolution in the experiments. We observe that for the same core size and for increasing shell thickness, the energy of the optical transition decreases, as expected due to quantum confinement effects. In addition, the reorganization energy, which is a measure of

the strength of exciton-phonon couplings, also decreases with increasing shell thickness and increasing core size,[193, 235] as the exciton phonon coupling $V_{n,n}^\alpha$ decreases faster than the increase of phonon densities.[109, 239, 240] As a result, the widths of both the ZPL and the LO phonon sideband decrease for larger-core and thicker-shell NCs, but the effect is somewhat more pronounced for the ZPL.

Panel (b) of Fig. 3.12 shows the dependence of the zero-phonon linewidth on the shell thickness and the reorganization energy, respectively. The reorganization energy correlates with measured Stokes shifts,[101, 235, 245] and thus, can also be inferred from experiments. At 100K, the zero-phonon linewidth decreases by $\sim 6\text{meV}$ as the shell thickness increases from 2 to 5 monolayers for both core sizes and seems to saturate beyond $\sim 5 - 6$ monolayers for the larger core. At 5K, the ZPL linewidth also shows a similar linear dependence on the reorganization energy, with a less steep slope and smaller change in FWHM ($2 - 3\text{meV}$ as the shell thickness increases). Given that the first-order exciton-phonon coupling dominates the dephasing rate $1/T_2$ below $T_c \approx 200\text{K}$, the near-linear dependence of the FWHM on the reorganization energy at 100K and 5K can be explained by Eq. (3.21) where the first-order dephasing rate depends linearly on reorganization energy.

As a summary, we developed a new atomistic theoretical model to calculate the photoluminescence spectra of CdSe/CdS core-shell nanocrystals and compared our prediction with single-molecule PL measurements for a wide range of temperatures. Our approach utilizes an atomistic force field to model the phonon modes, and the semiempirical pseudopotential model combined with the Bethe-Salpeter Equation to describe the excitonic structure and the exciton-phonon couplings to lowest order in the phonon modes in NCs. Our model overcomes the barrier of computational cost, enabling the first accurate atomistic calculation of PL spectra of NCs of experimentally relevant sizes. Using linear response theory, we showed that the calculated results accurately reproduce our measured PL spectra below a crossover temperature, $T_c \sim 200\text{K}$. In the low-temperature regime, our model explains the nature of the narrow, slightly-asymmetric zero-phonon line. By analyzing the coupling of individual phonon modes to the lowest bright exciton, we identified the specific acoustic and optical phonon modes that lead to the sidebands. Through direct comparison against experimental PL measurements, we validated the leading order exciton-phonon coupling terms derived from pseudopotential methods. As temperature increases above T_c , the measured zero-phonon linewidth increases more rapidly with temperature. Anharmonic atomic motion is examined and ruled out as the main source of further broadening in PL linewidth. We attributed this crossover behavior to the increasing significance of higher-order exciton-phonon coupling, which captures the frequency shifts and mode mixing of normal modes between the ground and excited states. We showed that including a second-order coupling term with a single parameter accounts for the behavior of the spectral linewidth above T_c , motivating future developments to calculate higher-order couplings from the pseudopotential model.

We applied our model to predict the behavior of the PL spectra for CdSe/CdS NCs of different core sizes and shell thicknesses and found that NCs with larger cores and thicker

shells have smaller overall exciton-phonon coupling, as demonstrated by their reorganization energies, as well as narrower ZPL and phonon sidebands. The theoretical approach established in this work is adaptable to a wide range of semiconductor NC materials and enables the first accurate atomistic modeling of PL spectroscopy for NCs of experimentally relevant sizes. The theoretical insights into the physical mechanisms giving rise to single-NC PL spectral features, such as ZPL width, phonon sidebands, and their dependence on NC structure, provides a lower bound to the ensemble-averaged spectral linewidth, assisting future designs of novel semiconductor nanocrystal materials for applications that require narrow emission linewidths.

Photoluminescence lineshape of GaAs nanocrystals

Having validated the DeepPseudopot pipeline for calculating excited-state properties combined with the linear-response framework for phonon-resolved emission spectra on well-studied CdSe/CdS core-shell nanocrystal systems, we are well-suited to use the model predictively. We therefore turn to colloidal GaAs quantum dots, where the molten-salt synthesis yields sufficiently high optical quality to resolve discrete excitonic transitions at the sub-100 meV energy range. Although fully resolved single-nanocrystal PL spectra at low temperatures remain experimentally challenging, theory can provide immediate microscopic insight into phonon mode couplings to band-edge excitons, how that coupling evolves with size, and how phonon sidebands intertwine with the fine structure of the lowest excitonic manifold.

Experimentally, phonon sideband information in GaAs QDs is accessed most directly through cryogenic fluorescence line-narrowing (FLN) and photoluminescence excitation (PLE) spectroscopy. PLE and FLN spectra were collected at 13 - 20 K from multiple GaAs/ZnS samples whose GaAs cores were synthesized over a range of temperatures (425 - 500 °C) to resolve discrete electronic transitions and identify phonon-related replicas. PLE spectra recorded at different emission wavelengths spanning the 610-750 nm range reveal multiple discrete absorption features above the band edge (Fig. 3.13a). In representative spectra detected near 660 nm emission (Fig. 3.13b), several optical transitions can be identified and assigned to higher hole states, with peaks labeled (b) - (d). By sweeping the detection wavelength, these features shift systematically, revealing the size dependence of each transition (Fig. 3.13c). The separations between transitions vary with GaAs QD size in the manner expected for quantum-confined states, and the transition energies match qualitatively with theoretical predictions of spin-resolved excitonic energies from DeepPseudopot and from an effective-mass model with finite barrier height. This comparison enables assignment of the observed PLE peaks to transitions involving the $1S_{3/2}$, $2S_{3/2}$, $1S_{1/2}$, and $3S_{3/2}$ hole levels. The exciton transition energy separations and their size dependence were also calculated using DeepPseudopot. The effective mass model and pseudopotential calculations both yield results consistent with the level ordering expected for GaAs QDs. We noticed a slightly better agreement for the higher-energy states from the pseudopotential calculation, which may reflect an overestimation of the transition energies by the effective mass method arising

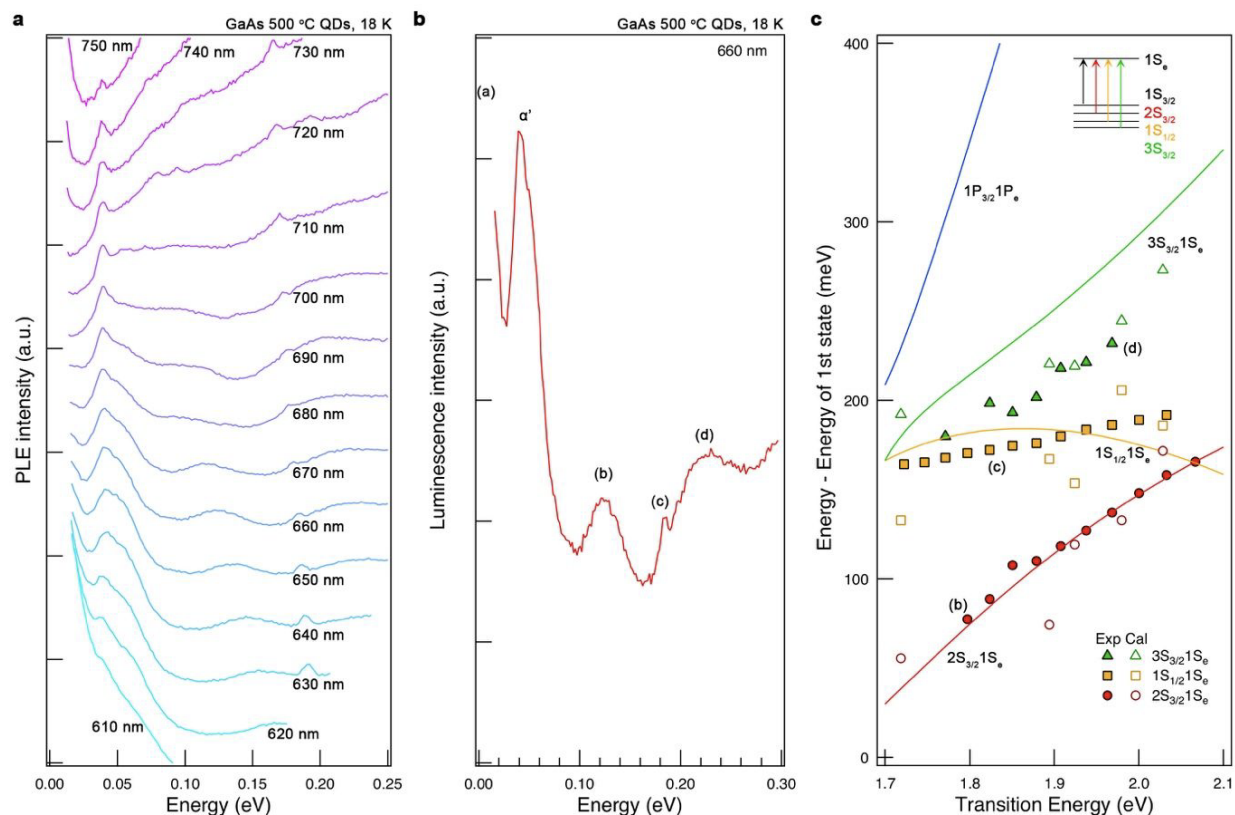


Figure 3.13: Optical transitions in GaAs/ZnS quantum dots. (a) Photoluminescence excitation (PLE) spectra recorded at 18 K for GaAs/ZnS QDs (GaAs cores synthesized at 500 °C) detected at emission wavelengths from 610 to 750 nm, revealing discrete excited-state transitions. (b) Representative PLE spectrum detected at 660 nm; peaks (b) - (d) correspond to transitions involving higher-energy hole states. (c) Transition energies extracted from PLE-versus-emission-energy curves with theoretical fits based on an effective-mass model (solid curves), and the DeepPseudopot model (hollow symbols). Inset: schematic of electron ($1S_e$) and hole ($1S_{3/2}$, $2S_{3/2}$, $1S_{1/2}$, $3S_{3/2}$) energy levels.

from the infinite potential barrier approximation for the hole. For comparison, analogous measurements on K_2S -treated GaAs cores without shells show the same general spectral features, although the weaker signal limits detailed analysis (Fig. 3.14). Somewhat surprisingly, within an energy window up to 0.3 eV above the $1S_{3/2}(h) \rightarrow 1S_e$ transition, we do not observe transitions associated with electron states from different momentum valleys (e.g., L -valley states), which have been suggested to become competitive under strong confinement in very small GaAs QDs. [246–249]

While Fig. 3.13 emphasizes the ladder of confined transitions over a broad excitation window, a more detailed view of the low-energy region within 100 meV of the band edge shows

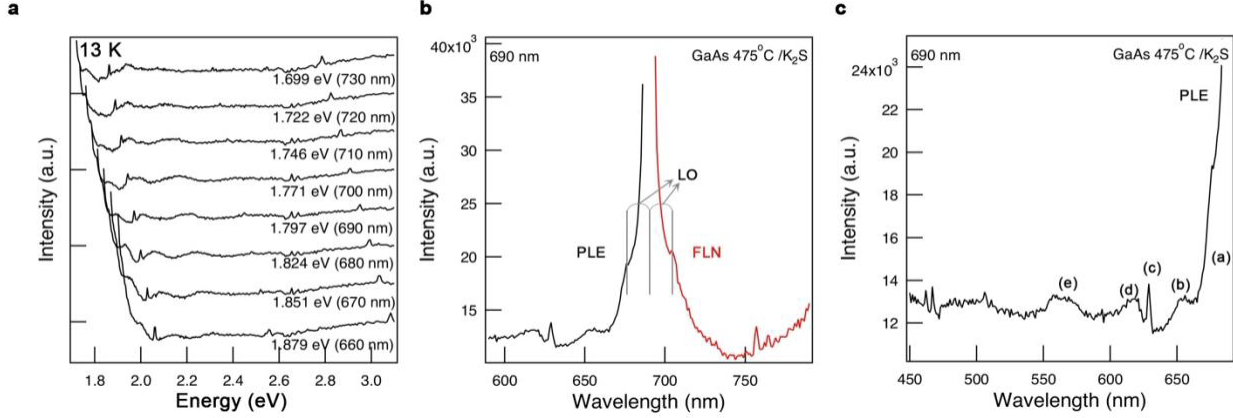


Figure 3.14: Exciton fine-structure analysis of GaAs/K₂S QDs. (a) PLE spectra at 13 K for GaAs QDs synthesized at 475 °C (black). (b) PLE and FLN spectra for GaAs/K₂S QDs (475 °C) with detection at 690 nm, showing the 37 meV LO-phonon replica. (c) Detailed PLE spectrum revealing multiple optical transitions labeled a–d.

both phonon replicas and excitonic fine-structure peaks within the same spectral window. In GaAs QDs emitting near 630 nm, representative FLN and PLE spectra reveal multiple features that can be grouped into two classes: LO-phonon replicas of the zero-phonon line (ZPL, labeled α) and additional exciton fine structure peaks (β_1 , β_2) (Fig. 3.15a). Distinguishing these contributions is essential because they encode different microscopic physics. Phonon replicas reflect coupling between an excitonic transition and specific vibrational modes, whereas fine-structure peaks reflect splittings within the lowest exciton manifold arising from exchange interactions. In practice, this motivates a combined theoretical treatment that captures both (i) realistic excitonic fine structure with spin-orbit coupling, and (ii) phonon-resolved lineshapes using exciton-phonon couplings computed from the same underlying atomistic Hamiltonian. The DeepPseudopot model, which explicitly includes spin-orbit coupling terms for III-V semiconductors, together with the linear-response formalism for phonon-resolved emission spectra, is well suited to address both requirements within a unified framework.

Consistent with this picture, Fig. 3.15a shows that the LO-phonon replica α' appears at a well-defined energy offset from the ZPL, while the additional features β_1 and β_2 track fine-structure splittings within the bright exciton manifold. To interpret the phonon replicas microscopically, we modeled phonon frequencies, exciton-phonon coupling (EXPC) strengths, and their size dependence using DeepPseudopot combined with a Tersoff-type force field, as discussed previously in this chapter. The calculated EXPC in GaAs QDs is highly structured (Fig. 3.16a). Most phonons couple weakly to the lowest exciton states, and only a few modes within the acoustic (< 20 meV), transverse optical (TO, between 20 and 38 meV) and longitudinal optical (LO, above 40 meV) manifolds dominate the coupling. The corre-

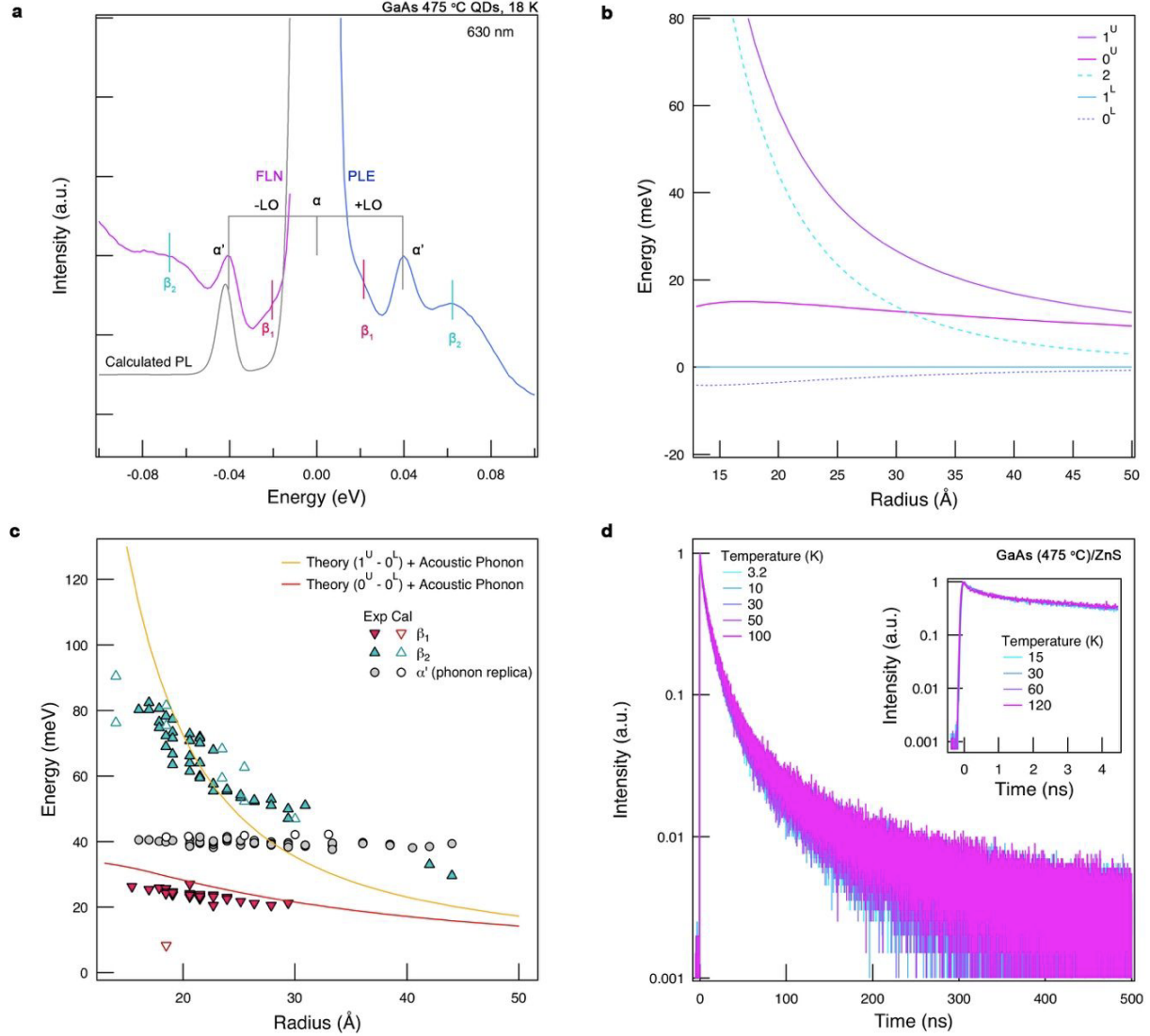


Figure 3.15: Exciton fine structure and recombination dynamics in GaAs/ZnS quantum dots. (a) Representative comparison of fluorescence line-narrowing (FLN, pink), PLE (cyan), and calculated PL (gray) spectra from GaAs/ZnS QDs emitting at 630 nm. The zero-phonon line (α) and its LO-phonon replica (α') are indicated, along with fine-structure features β_1 and β_2 . (b) Calculated exciton fine-structure energies as a function of QD radius, showing the evolution of bright ($\pm 1^U$, 0^U , $\pm 1^L$) and dark (0^L , ± 2) states. (c) Bright-state splitting energies: experimental values (circles) compared with theoretical predictions for the $\pm 1^U - 0^L$ (yellow) and $0^U - 0^L$ (red) transitions using the effective mass model, and DeepPseudopot model exciton fine structure calculations (hollow colored symbols). Gray crosses indicate LO-phonon replica positions and grey hollow circles indicate the LO phonon sideband locations calculated using the DeepPseudopot method. (d) Temperature-dependent photoluminescence decay spectra from 3.2 K to 100 K, showing negligible variation; inset shows the PL decay measured by a streak camera.

sponding phonon density of states is shown in Fig. 3.16b. Representative atomic motions for the strongest-coupled acoustic, TO, and LO modes are illustrated in Fig. 3.16c-e. This “sparse” coupling picture explains why phonon sidebands appear as a limited number of distinct features rather than as a broad, featureless shoulder. The acoustic phonon modes with the strongest coupling to band-edge excitons have frequencies that scale inversely with QD size, whereas the LO phonon frequencies show minimal size dependence, consistent with their bulk-like Ga-As relative optical vibration.

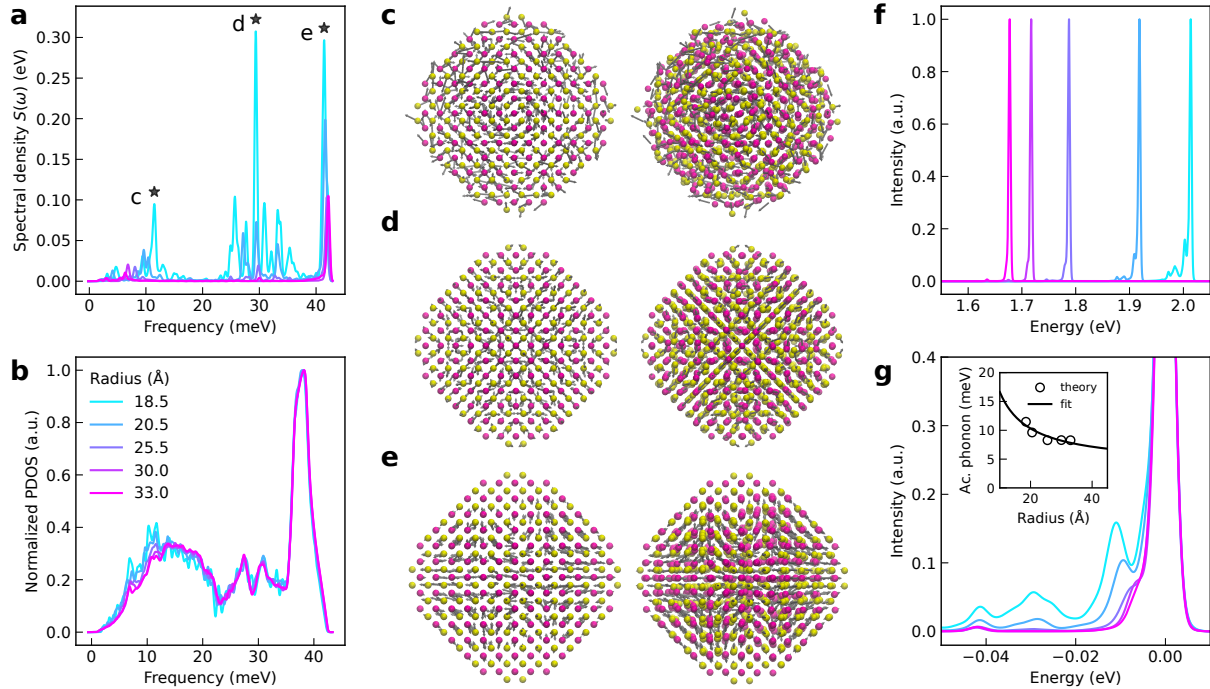


Figure 3.16: Theoretical modeling of exciton-phonon coupling and phonon-resolved single-QD PL spectra of GaAs QDs. (a) Calculated spectral densities depicting exciton-phonon coupling (EXPC) strengths for GaAs QDs with diameters of 3.7, 4.1, 5.1, 6.0, and 6.6 nm, showing the size dependence. The phonon modes with the strongest coupling strengths are labeled and correspond to panels (c)-(e). (b) Normalized phonon density of states (PDOS) of GaAs QDs. (c)-(e) Atomic motions of the acoustic, transverse optical (TO), and longitudinal optical (LO) phonon modes of the 3.7 nm GaAs QD with the strongest EXPC strengths. Colors: As - yellow; Ga - magenta. (f) Calculated single-QD PL emission spectra at 18 K using DeepPseudopot, showing size-dependent band-gap energies ranging from ~ 2.0 to ~ 1.65 eV. (g) Shifted single-QD PL spectra highlighting the size dependence of the acoustic-phonon sidebands. Inset: acoustic-phonon energy versus QD radius from theory (circles) and an analytical fit (line), demonstrating the expected $1/R$ dependence for confined acoustic-phonon energies.

The single-NC photoluminescence (PL) emission spectra were computed at low temperatures (5 K) using linear-response theory. [127, 220] A Gaussian broadening of 4 meV was included to account for the finite spectral resolution of the experimental spectrometer and spectral diffusion effects. Thermal population of the initial excitonic states was modeled using a Boltzmann average over the lowest ten excitonic states. At low temperatures, the calculated spectra show an LO-phonon replica at ~ 42 meV from the ZPL, which is consistent with the FLN and PLE measurements. A secondary lower-energy acoustic-phonon shoulder at $\sim 7 - 13$ meV arises from modes with collective nuclear vibrations extending across the entire nanocrystal, such as twisting- or breathing-like distortions, but it is not resolved in FLN or PLE due to its small energy spacing from the excitation source. Together, these results demonstrate that exciton-phonon interactions in GaAs NCs are governed by a small number of phonon modes and give rise to distinct and well-resolved features in PL spectra.

As the GaAs QD size increases, the excitonic gap, phonon frequencies, and EXPC evolve systematically. The acoustic, TO, and LO phonons with the strongest coupling strengths, together with their associated atomic motions, are extracted from the spectral densities and analyzed. Acoustic-phonon frequencies scale inversely with size, whereas optical-phonon frequencies show minimal size dependence, consistent with their origin as intrinsic cation-anion relative motion within the GaAs bulk lattice. Although EXPC in GaAs QDs generally decreases with increasing size, coupling to phonon modes in the 24 - 38 meV range, which are attributed to TO phonons in GaAs, weakens most rapidly and ultimately disappears in larger QDs. This behavior contrasts with the LO and acoustic modes and reflects the stronger sensitivity of TO-phonon EXPC to quantum confinement. The size dependence of the coupling directly reshapes the single-QD PL line shapes. At low temperatures, where the spectral resolution resolves clear phonon sidebands, increasing QD size leads to a systematic reduction of phonon sideband intensity relative to the ZPL and a progressive simplification of the spectra. Higher-energy replicas in the 24 - 38 meV range corresponding to TO phonons disappear entirely for larger QDs.

Collectively, the combined FLN/PLE measurements and phonon-resolved theoretical modeling establish a consistent microscopic picture for colloidal GaAs QDs in the strong-confinement regime. PLE resolves a ladder of discrete excitonic transitions. FLN/PLE phonon replicas reveal bulk-like LO phonon modes and size-dependent acoustic contributions. Theoretical modeling explains both the sparsity and the size dependence of EXPC, including the progressive simplification of the emission spectrum with increasing size. These results provide a foundation for future single-nanocrystal PL experiments and more refined modeling of the interplay between exciton fine structure and phonon coupling in GaAs quantum dots.

A natural future extension of this chapter is to move beyond the linear (first-order) exciton-phonon picture and systematically incorporate second-order (quadratic) vibronic couplings when interpreting fine spectral structure and temperature-dependent PL lineshape asymmetries. As suggested by the results in the chapter, quadratic terms can open additional dephasing and mode-mixing channels that are weak at cryogenic temperatures yet become increasingly consequential as phonon populations grow, potentially reshaping both the ho-

ogeneous linewidth and the detailed balance between the zero-phonon line and phonon sidebands. Future work could therefore focus on extending the effective vibronic Hamiltonian and corresponding correlation-function treatments to include a more complete set of second-order contributions (e.g., state-dependent frequency renormalization and mode-rotation effects). [250] On the experimental side, this direction motivates targeted comparisons against single-particle PL across temperature, shell composition, and applied strain, where subtle asymmetries and crossover behaviors are especially diagnostic. Taken together, these developments would further strengthen the predictive connection between microscopic exciton-phonon interactions and macroscopic optical observables, while keeping the detailed methodological elaboration appropriately deferred to a dedicated study.

3.3 Alloyed III-V nanocrystals: composition-tuned electronic character

Introduction and motivation

As introduced in Chapter 1, the $\text{In}_{1-x}\text{Ga}_x\text{P}$ alloy system provides a continuously tunable platform for studying the evolution from direct-gap to indirect-gap behavior under quantum confinement. Molten-salt cation exchange enables independent control over nanocrystal size and alloy composition, overcoming the limitations of epitaxial approaches where strain couples these two degrees of freedom. However, prior attempts at colloidal $\text{In}_{1-x}\text{Ga}_x\text{P}$ synthesis via conventional solution routes have not unambiguously demonstrated uniform gallium incorporation into the InP lattice. [251, 252] The molten-salt approach starts from well-characterized InP nanocrystals dispersed in a gallium-containing molten salt, where high-temperature annealing drives solid-state In-to-Ga interdiffusion, and results in a more controlled route to homogeneous alloyed nanocrystals. [90, 91, 96] The high thermal stability and rigorously oxygen-free environment of the molten-salt medium further enable the study of $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals without oxidation artifacts from ligand decomposition or atmospheric contamination.

In this section, we analyze the optical properties of a series of $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals with gallium fractions from $x = 0$ to 0.92. To fully exploit the oxygen-free nature of the molten-salt-derived surface, a ZnS shelling protocol was developed that rigorously avoids oxygen-containing precursors. Optoelectronic characterization via time-resolved PL and transient absorption spectroscopy on the resulting $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ nanocrystals reveals that the oscillator strength of the emissive state decreases with increasing gallium content, and that the excitonic bleach feature disappears for samples with >65% gallium, consistent with conversion to indirect-gap behavior. Atomistic semi-empirical pseudopotential calculations successfully capture these trends, showing good agreement with measured optical gaps, absorption spectra, and radiative lifetimes, and revealing the Γ - to X -valley transition in the conduction band-edge states as composition increases.

An In-to-Ga cation exchange reaction on InP nanocrystals in molten salts provides a practical route to otherwise difficult-to-access ternary III-V $\text{In}_{1-x}\text{Ga}_x\text{P}$ phases.[90, 96] As summarized schematically in Fig. 3.17A, the synthetic strategy relies on replacing the native long-chain ligands of the InP cores with compact inorganic Z-type gallium halides, which enable dispersion in molten-salt media while avoiding the introduction of unwanted heteroatom impurities such as chalcogenides. [91, 96] Because gallium is strongly oxophilic at elevated temperatures, oxygen-containing ligands must be avoided throughout recovery and subsequent shell growth; accordingly, we employ an amine-based recovery protocol that preserves colloidal processability without carboxylates and helps suppress surface oxidation. To demonstrate the generality of this route, we apply it to three InP nanocrystal populations of different sizes and surface chemistries, including TOP/TOPO-capped particles prepared by dehalosilylation, [253, 254] smaller indium-myristate-derived particles,[255] and

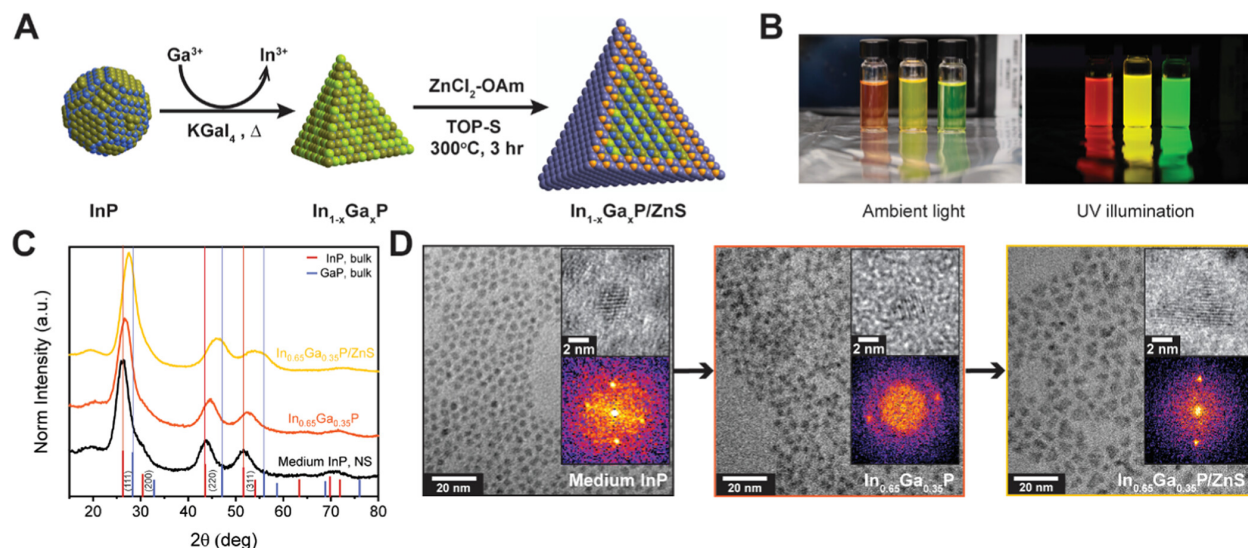


Figure 3.17: (A) Reaction scheme for In-to-Ga cation exchange and subsequent ZnS shell growth. (B) Photographs of emissive core-shell $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ samples with similar gallium contents, prepared from 4.9 nm InP (red-emitting after cation exchange), 4.0 nm InP (yellow), and 3.2 nm InP (green) starting populations. (C) Representative powder X-ray diffraction (XRD) patterns indicate a zinc blende crystal structure for the cores and for the core-shell samples derived from the 4.0 nm InP particles. (D) Transmission electron microscopy (TEM) images showing the evolution of particle morphology during cation exchange and shell growth.

an intermediate-sized commercial population. After ligand exchange with GaI_3 , annealing in KGaI_4 (Fig. 3.17A), and amine-assisted recovery, X-ray diffraction confirms retention of the zinc-blende phase in the alloyed cores and in the corresponding core-shell products (Fig. 3.17C), while Le Bail refinement allows gallium compositions to be assigned. Larger nanocrystals require more aggressive annealing to reach similar Ga incorporation, consistent with their greater resistance to cation exchange, and additional low- 2θ features in the smaller samples likely arise from ligand ordering. [256]

A second motivation for this design is that Ga incorporation not only tunes the alloy composition but also decreases the core lattice constant, improving compatibility with ZnS shell growth and enabling efficient surface passivation for photophysical studies. As shown in Fig. 3.17A, we therefore use an oxygen-free, reducing ZnS shelling protocol based on ZnCl_2 in oleylamine and trioctylphosphine sulfide. The resulting $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ nanocrystals span red, yellow, and green emission across the large-, medium-, and small-core samples, respectively, at similar alloy compositions near $x \sim 35\%$ (Fig. 3.17B), reflecting the expected role of quantum confinement in tuning the band gap while holding composition approximately fixed. Representative $\text{In}_{0.65}\text{Ga}_{0.35}\text{P}/\text{ZnS}$ nanocrystals derived from 4 nm InP exhibit a 60 nm

PL FWHM and PLQY of 75%, while green-emitting $\text{In}_{0.66}\text{Ga}_{0.34}\text{P}/\text{ZnS}$ samples derived from 3.2 nm InP reach $\sim 48\%$ PLQY without further optimization; by contrast, the larger-particle samples are less emissive ($\sim 19\%$ PLQY), consistent with prior evidence for higher internal defect densities in this synthetic route. [96] The shell nevertheless provides substantial passivation despite a residual lattice mismatch of $\sim 5.5\%$ between $\text{In}_{0.65}\text{Ga}_{0.35}\text{P}$ and ZnS, as evidenced by peak narrowing and shifts to higher 2θ after shelling in Fig. 3.17C. In parallel, TEM images show that cation exchange increases particle faceting and that subsequent shell growth yields representative faceted $\text{In}_{0.65}\text{Ga}_{0.35}\text{P}/\text{ZnS}$ nanocrystals with an estimated edge length of 9 nm, corresponding to roughly two ZnS monolayers (Fig. 3.17D). Together, these results establish the synthetic and structural basis for the photophysical analysis and theoretical modeling presented in the following section.

Evolution of optoelectronic properties as a function of Ga composition

Equipped with an oxygen-free shelling protocol that yields good-quality emissive samples, we next seek to understand how the optoelectronic properties of these core-shell samples evolve as a function of gallium composition. Starting with the 4 nm InP nanocrystals, we synthesized a series of alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals by performing In-to-Ga cation exchange in a KGaI_4 molten-salt reaction medium under different combinations of annealing temperature and duration. The amine-capped $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals were recovered as a colloidal solution in toluene and characterized via X-ray diffraction; subsequently, the gallium compositions were estimated to be between 14 and 60% (see Fig. 3.18A). We performed elemental analysis using X-ray fluorescence (XRF) on the $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ core-shell samples. For each sample, the elemental analysis method estimates the gallium content at $\sim 25\%$ higher than that estimated by employing XRD measurement of the lattice constant and subsequent Vegard's law interpolation of the gallium content. The 4 nm diameter QDs used in this study have approximately 25% of their atoms at the surface. Thus, one can imagine that changes in the composition of the outer surface layer can dramatically change the QD composition with only a minor impact on the QD interior. For example, if a surface monolayer of metal-rich InP exchanges to GaP, the elemental composition could be up to 25% gallium, while the XRD pattern would show only minor changes, resulting primarily from the surface strain rather than bulk lattice reorganization. As expected, absorption peaks shift monotonically to higher energies with an increasing gallium content, indicative of a widening band gap. Notably, we observe a continuous decline in the sharpness of the excitonic feature with an increasing gallium content (Fig. 3.18B). We can attribute this observation either to the broadening of nanocrystal size distribution over the course of high-temperature annealing or to the mixing of excitonic states from direct and indirect valleys in the conduction band. Photographs of the particles under UV illumination (Fig. 3.18C) show that we can achieve bright emission in a wide range of colors between red and green by varying gallium compositions between 0% and 58% for 4 nm diameter cores. The recorded PL spectra corroborate our visual

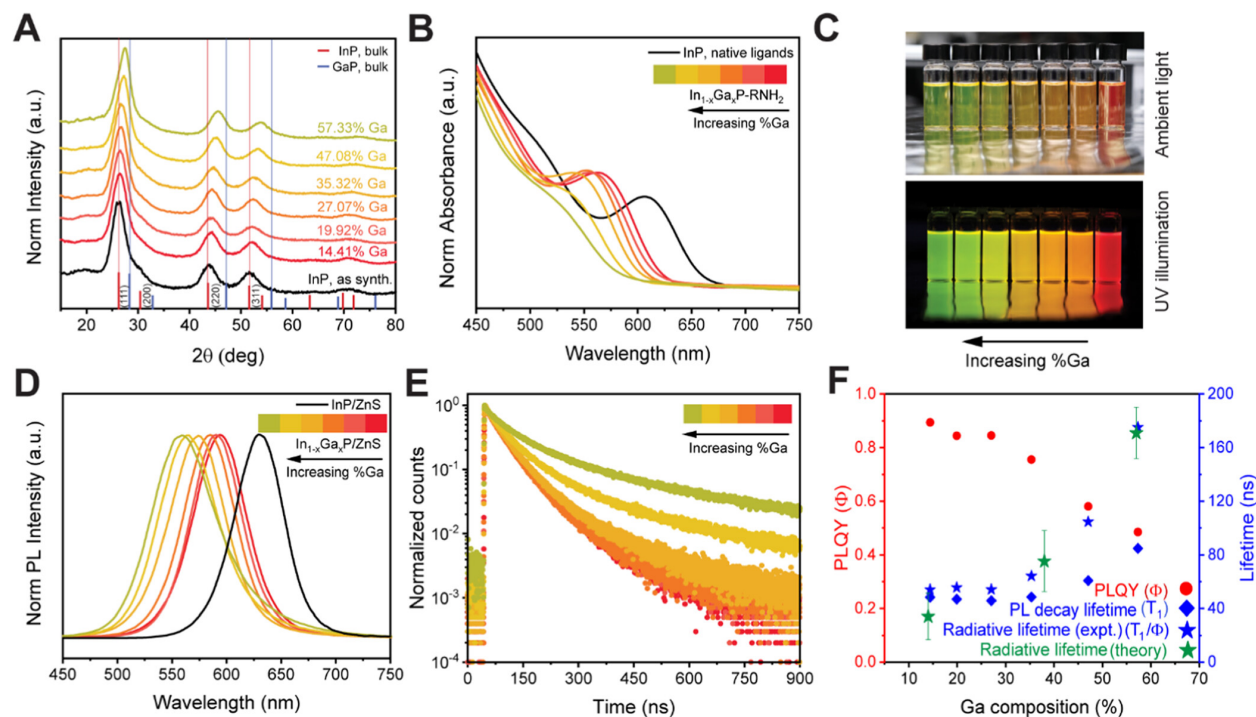


Figure 3.18: (A) Powder X-ray diffraction patterns of $\text{In}_{1-x}\text{Ga}_x\text{P}$ cores derived from 4.0 nm InP nanocrystals. (B) Absorption spectra of the alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ cores, normalized at 400 nm, showing a diminished excitonic feature and a blue-shifted absorption onset with increasing gallium composition. (C) Photographs of core-shell $\text{In}_{1-x}\text{Ga}_x\text{P/ZnS}$ samples with varying gallium contents, all derived from the same 4.0 nm InP nanocrystals, showing a broad range of emission colors; red emission corresponds to the InP/ZnS sample with $x = 0$. (D) Corresponding emission spectra. (E) Time-resolved PL dynamics integrated over the emission spectra, showing longer decay lifetimes at higher gallium content. (F) Trends in PLQY, the time constants associated with the dominant excitonic decay channel, and the corresponding radiative lifetime. Calculated radiative lifetimes for $\text{In}_{1-x}\text{Ga}_x\text{P}$ quantum dots with random gallium distributions agree well with experiment. Trace colors in panels (B), (D), and (E) are the same as in panel (A).

observations: a blue shift of the emission peak accompanies the increasing gallium content (Fig. 3.18D).

To quantitatively rationalize the experimentally observed optoelectronic properties of $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs, the electronic structure and optical properties of alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs are calculated using atomistic semi-empirical pseudopotential methods [150, 158, 160, 257] combined with the Bethe-Salpeter equation (BSE). [135, 219] To yield a unified description of inter-atomic interactions in the alloyed systems, single atomistic traditional pseudopotentials each for In, Ga, P, and As were fitted to accurately reproduce the bulk band structures and

bulk deformation potentials of relevant binary semiconductors (i.e., InP, GaP, InAs, and GaAs). We used pseudopotentials with a local form in the reciprocal space with six fitting parameters $\{a_0, a_1, a_2, a_3, a_4, a_5\}$:

$$\tilde{v}_\mu(q) = a_0 \left(1 + a_4 \text{Tr } \epsilon_\mu + a_5 (\text{Tr } \epsilon_\mu)^3\right) \frac{q^2 - a_1}{a_2 \exp(a_3 q^2) - 1}. \quad (3.23)$$

where $\tilde{v}_\mu(q)$ is the pseudopotential around atom μ (In, Ga, P, or As) in the reciprocal space. ϵ_μ is the local strain tensor around atom μ , and its trace is calculated using the tetrahedron volume formed by the nearest neighbors. Parameters a_0 through a_3 were fitted to the bulk band structures of InAs, InP, GaAs, and GaP obtained through high-accuracy electronic structure calculations by Cohen et al. [157, 258]. The local strain-dependent prefactors (a_4 and a_5) were fitted to reproduce the literature bulk deformation potentials of the CBM and VBM for each semiconductor material. [165]

The parameters for fitted pseudopotentials of As, Ga, In, and P are summarized in Table 3.3. The a_5 parameter for the cubic strain tensor term is only needed for Ga to give well-fitted results to the bulk deformation potentials of Ga-containing binary semiconductors. Fig. 3.19 shows the bulk band structures and deformation potentials generated from our pseudopotentials as compared to literature, in good quantitative agreement.

Table 3.3: The a_0 through a_5 parameters for the best-fit atomistic pseudopotentials of As, Ga, In, and P. See Eq. S1 for the functional form of the pseudopotential.

	a_0	a_1	a_2	a_3	a_4	a_5
As	25.68513132	2.69329915	1.63958593	0.49218946	0.01647533	0
Ga	48.55247982	2.28309682	3.77112430	0.45685179	0.56676447	8.09704232
In	50.52631742	1.98680525	3.15524320	0.43784813	0.36378779	0
P	28.76635710	2.67994632	1.78491672	0.46023571	-0.00357477	0

To construct the alloyed QD geometries, an initial tetrahedral InP nanocluster was cut from the bulk zincblende InP configuration with In atoms as the surface terminations. The edge lengths of these tetrahedrons were chosen to match the sizes of the experimentally synthesized QDs. Since the $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs are experimentally synthesized from spherical InP QDs, we converted the diameter (d) of the spherical InP QD to the edge length (a) of the tetrahedral $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs by equating their volumes. Thus, the tetrahedral $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs constructed from 4.0 nm diameter InP QD have edge lengths of around 6.6 nm.

Next, In cations were randomly selected from the initial configuration and replaced with Ga cations. The number of In-to-Ga exchanges was calculated by the desired Ga percentage (14%, 38%, 57%, 65%, 78%, 92%, and 100%). For each Ga composition, three different random In-to-Ga exchanges were considered. $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs with inhomogeneous gallium distribution were also considered. See the end of this subsection for detailed descriptions.

To account for the local strain effects due to the cation exchange, the structures were then relaxed using the conjugate gradient descent algorithm implemented in LAMMPS. The

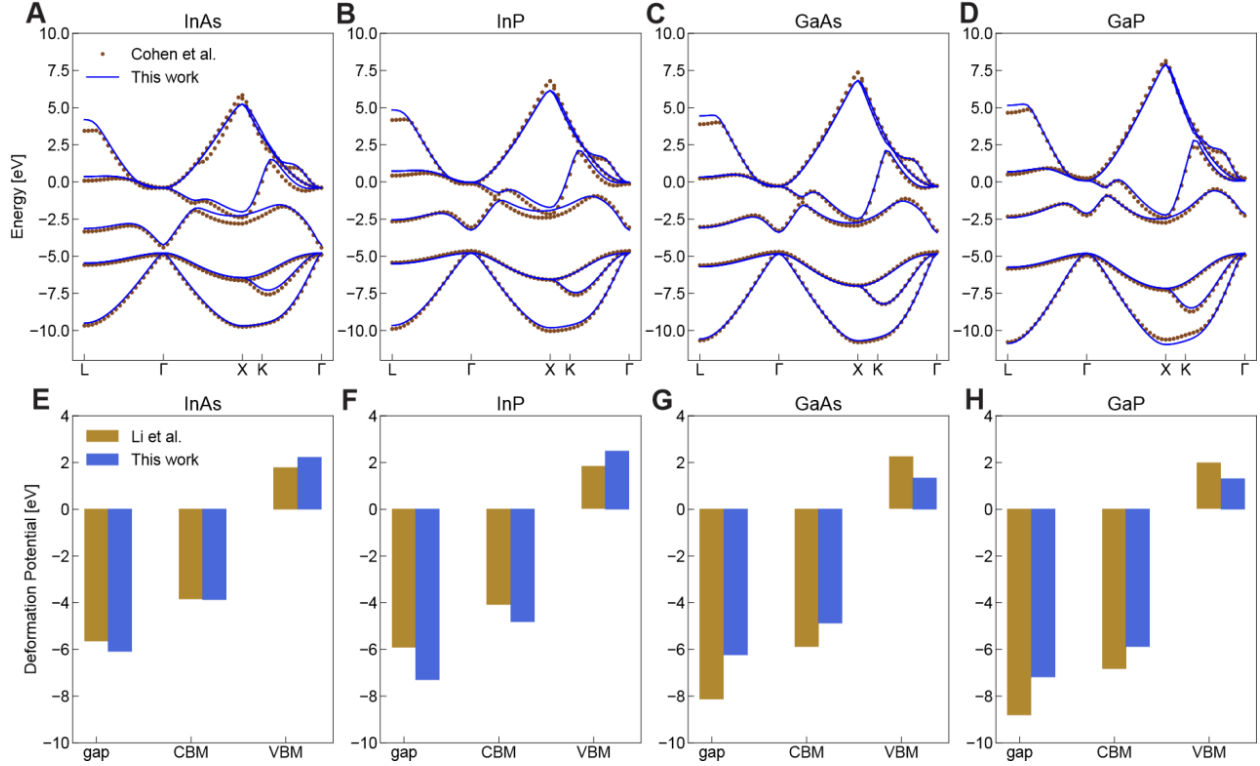


Figure 3.19: Bulk band structures (A-D) and deformation potentials (E-H) calculated using the fitted pseudopotentials of this work (blue lines and bars), compared with literature values for the corresponding bulk properties (gold dots and bars) [157, 165, 258] of the binary semiconductors InAs, InP, GaAs, and GaP.

Tersoff-type classical force field previously parameterized for the III-V semiconductors of interest was used for the energy minimization. [187] Lastly, the singly-bonded P atoms at each of the four corners of the tetrahedron were removed, and the QD was passivated with ligand potentials.

The relevant $\text{In}_{1-x}\text{Ga}_x\text{P}$ structures are tabulated in Table 3.4. The geometry of an $\text{In}_{0.35}\text{Ga}_{0.65}\text{P}$ constructed from 4.0 nm InP QD with random gallium distribution is shown in Fig. 3.20.

In addition to uniformly distributed Ga, alloyed QDs with Ga-rich centers or Ga-rich exteriors were also constructed and calculated. In these cases, at the step of the QD construction where In cations were replaced with Ga, the cations were categorized into the “center” and the “exterior” by the sphere that inscribes tetrahedron. Random In-to-Ga replacements were then carried out in each section, with a higher Ga concentration within (or outside of) the inscribed sphere. The rest of the theoretical treatments remain the same.

Calculated optoelectronic properties of $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs with inhomogeneous Ga distribu-

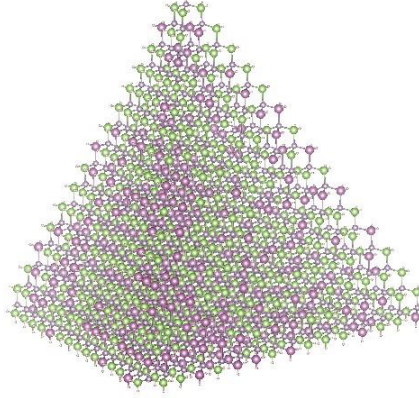


Figure 3.20: Atomic configuration of the $\text{In}_{0.35}\text{Ga}_{0.65}\text{P}$ quantum dot used in the electronic structure calculations. The alloyed quantum dot was generated from a 4.0 nm InP nanocrystal through random In-to-Ga cation exchange. For visual clarity, the pseudo-ligands used for surface passivation in the atomistic pseudopotential calculations are represented as H atoms. Color scheme: pink, In; green, Ga; purple, P; white, H.

Table 3.4: Relevant tetrahedral $\text{In}_{1-x}\text{Ga}_x\text{P}$ quantum dot structures constructed from a 4.0 nm InP spherical quantum dot and used in the calculations of this work. The numbers of In, Ga, and P atoms for each gallium content are listed.

Structure	In atoms	Ga atoms	P atoms
Spherical InP	727	0	736
$\text{In}_{0.86}\text{Ga}_{0.14}\text{P}$	829	136	816
$\text{In}_{0.62}\text{Ga}_{0.38}\text{P}$	597	368	816
$\text{In}_{0.43}\text{Ga}_{0.57}\text{P}$	417	548	816
$\text{In}_{0.35}\text{Ga}_{0.65}\text{P}$	339	626	816
$\text{In}_{0.22}\text{Ga}_{0.78}\text{P}$	211	754	816
$\text{In}_{0.08}\text{Ga}_{0.92}\text{P}$	78	887	816
GaP	0	965	816

tions (particularly the Ga-rich surface QDs) show qualitative deviations from experimental measurements in this work, further reaffirming the homogeneous alloying of cations during the cation exchange synthesis step. As shown in Fig. 1.3, the calculated optical gap of $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs with Ga-rich surfaces is very different from those calculated for the homogeneous gallium distributions as well as the experimental observations. Further, as shown below in Fig. 3.21, the oscillator strength and absorption spectra are also qualitatively different for QDs with Ga-rich surfaces, manifesting in a different first peak energy and more

pronounced higher energy peaks. These theoretical results of optoelectronic properties corroborate the experimental evidence from ssNMR that homogeneous gallium alloying occurs in the $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs in this work.

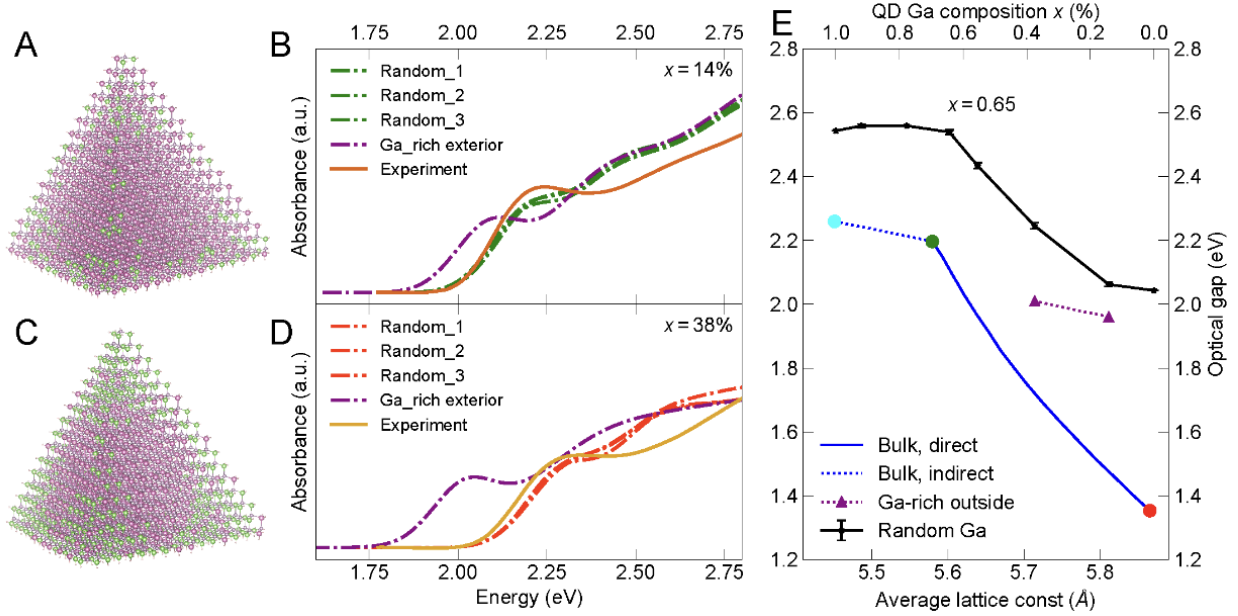


Figure 3.21: (A,C) Atomic structures of $\text{In}_{1-x}\text{Ga}_x\text{P}$ quantum dots with Ga-rich exteriors for $x = 14\%$ and $x = 38\%$. (B,D) Calculated absorption spectra (dash-dotted lines) of $\text{In}_{1-x}\text{Ga}_x\text{P}$ quantum dots with gallium compositions of $x = 14\%$ and $x = 38\%$, compared with the corresponding experimental spectra (solid lines). For the theoretical calculations, results are shown for three quantum dots with spatially random gallium distributions and one quantum dot with a Ga-rich exterior. (E) Optical gaps of $\text{In}_{1-x}\text{Ga}_x\text{P}$ quantum dots with spatially random gallium distributions and with Ga-rich exteriors, compared with the band gaps of the corresponding bulk alloys.

Given the relaxed QD geometry, the fitted pseudopotentials were Fourier transformed into the real-space form and used to construct the single quasiparticle Hamiltonian in the non-interacting electron picture:

$$\hat{H}_{\text{qp}} = -\frac{1}{2}\nabla^2 + \sum_{\mu} \hat{v}_{\mu}(\mathbf{r} - \mathbf{R}_{\mu}). \quad (3.24)$$

where $\hat{v}_{\mu}(\mathbf{r})$ is the pseudopotential around atom μ in the real space. The stochastic filter diagonalization technique was then used to obtain the electron states $\phi_e(\mathbf{r}_e)$ and hole states $\phi_h(\mathbf{r}_h)$ of the QD near its band edge. The real-space grid spacing of 0.8 Bohr was sufficient to converge the solutions. The quasiparticle eigenstates were then used as linear combinations

of electron-hole product wavefunctions, and the coefficients c_{ai}^n were obtained by solving the Bethe-Salpeter equation within the static screening approximation and the Tamm-Dancoff approximation:

$$\psi_n(\mathbf{r}_e, \mathbf{r}_h) = \sum_{a,i} c_{ai}^n \phi_e(\mathbf{r}_e) \phi_h(\mathbf{r}_h). \quad (3.25)$$

where a and i are electron and hole state indices, respectively. All the BSE calculations were converged to 0.001 eV with the linear combination of 60 electron states and 100-200 hole states, depending on the size of the alloyed QD. The dielectric constants for the alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs were chosen to be the same as the InP QDs of the same size. [159, 189, 259] Given the similar bulk static dielectric constants for InP and GaP, gallium composition is assumed to have a negligible effect on the dielectric constants of the alloyed QDs. For alloyed QDs synthesized from 4.0 nm InP, the dielectric constant of $\epsilon = 11.45$ was used.

The oscillator strength for each exciton transition was calculated following the equation given in the main text, where the dipole moment μ_n for exciton n was calculated using the quasiparticle wavefunctions and the BSE coefficients:

$$\mu_n = \sum_{a,i} c_{ai}^n \langle \phi_e | \mathbf{r} | \phi_h \rangle. \quad (3.26)$$

The absorption spectrum was calculated using the exciton energies and oscillator strength and broadened with Gaussian functions to reflect the inhomogeneity arising from size dispersion, as shown in Eq. 3.27:

$$I(\omega) = \sum_n \frac{f_n}{\Gamma_n \sqrt{2\pi}} \exp \left[-\frac{(\omega - E_n)^2}{2\Gamma_n^2} \right]. \quad (3.27)$$

where E_n and f_n are the energy and oscillator strength for exciton n . E_g is the bulk material gap, which is interpolated between $E_g(\text{InP}) = 1.34$ eV and $E_g(\text{GaP}) = 2.27$ eV for alloyed QDs. $\Gamma_n \propto E_n - E_g$ is the energy-dependent inhomogeneous broadening. [59]

The radiative lifetimes were calculated using the equations given in the main text. As stated in the main text, the total rate given in Eq. 3.28 is given by a canonical average over the Boltzmann distribution of excitonic states:

$$\frac{1}{\tau_{r,\text{tot}}} = \sum_n \frac{1}{\tau_{r,n}} \frac{e^{-\beta(E_n - E_0)}}{Z}. \quad (3.28)$$

where

$$Z = \sum_n e^{-\beta(E_n - E_0)} \quad (3.29)$$

is the partition function. The results for the alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs are tabulated, with multiple entries corresponding to different random Ga-distributions during the construction of the QDs.

Our theoretical approach allows for joint investigations and direct comparisons between theory predictions and experimental measurements as it permits accurate atomistic calculations of the optoelectronic properties for $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals with arbitrary gallium composition with experimentally relevant sizes. Electronic structure calculations confirm the experimentally observed peak shifts. The calculated optical gaps for $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs show a monotonic increase in energy with higher gallium concentration and a similar dependence on the average lattice constant as compared to the bulk alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$. The vertical shift of the optical gap between the QDs and bulk ternary alloys is attributed to the confinement energy of QD systems. The slope of the QD optical gap changes at 65% gallium composition, indicating an equivalent transition between direct- and indirect-gap regimes as in the bulk alloy $\text{In}_{1-x}\text{Ga}_x\text{P}$. And the shift of the transition point from 75% in the bulk to 65% for 4 nm QDs can be explained by the quantum confinement and the much smaller electron effective mass in the Γ valley as compared to the effective mass in the X and L valleys. In addition, spatially inhomogeneous In-to-Ga cation exchange is studied through theoretical calculations. The calculated optical properties (namely, optical gap, oscillator strengths, and absorption spectra) for QDs with Ga-rich surfaces differ largely from experimental and theoretical results for QDs with spatially random Ga distributions. These results are consistent with our ssNMR studies, suggesting that Ga is homogeneously distributed in the particle.

We carried out steady-state absorption and PL spectroscopy on each sample (Fig. 3.18B, D). $\text{In}_{0.86}\text{Ga}_{0.14}\text{P}/\text{ZnS}$ is the brightest sample among the alloyed populations, registering a quantum yield of 89% along with good color purity (57 nm FWHM of the emission peak). For the 4 nm nanocrystals studied so far, it is difficult to incorporate larger amounts of gallium ($x > 58\%$) due to high-temperature decomposition. However, we analyzed all possible gallium compositions computationally for 4 nm diameter $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals by calculating the absorption spectra of InP QD, GaP QD, and alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs ranging from 14 to 92% gallium content using the atomistic pseudopotential methods, as shown in Fig 3.22A-H. To generate the absorption spectra, the oscillator strength

$$f = \frac{4m_e E}{3\hbar^2 e^2} |\boldsymbol{\mu}|^2 \quad (3.30)$$

(where $\boldsymbol{\mu}$ is the transition dipole moment and E is the exciton energy) for each excitonic state is calculated. For all of the samples with gallium content below 57%, the majority of the low energy states in the density of states (DOS) have large oscillator strength, consistent with the strong excitonic emission observed for each excitonic transition. [260]

For $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs with $x > 57\%$, the computation results show a continued decrease in the sharpness of the absorption onset as the gallium content increases Fig 3.22E-H. The decrease in the magnitude of the absorption onset is a result of the decrease in oscillator strength of the lowest-energy excitonic transitions, consistent with indirect-like electronic transitions. This shows that extensive gallium exchange creates many low-energy “dim” excitonic states at the band edge, which is indicative of optical transitions with a more “indirect” character.

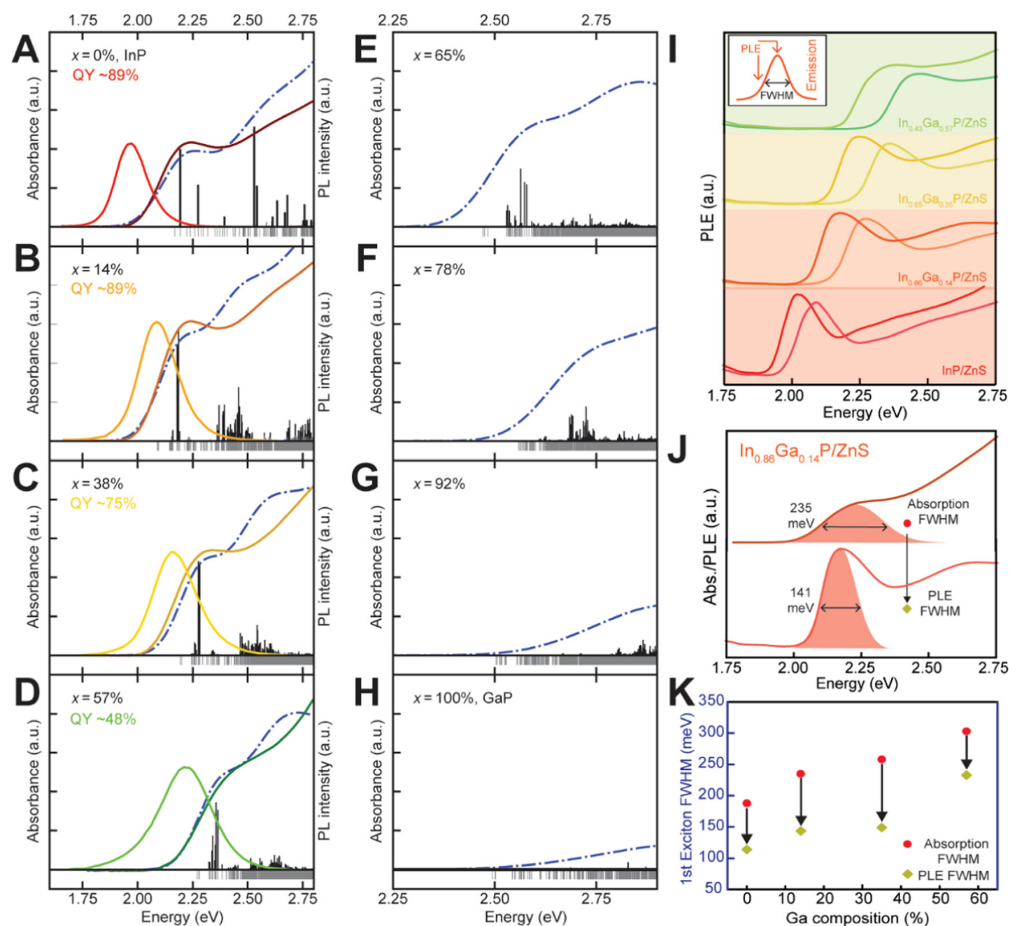


Figure 3.22: (A-H) Experimental absorption and emission spectra (solid colored lines), together with calculated absorption spectra (blue dash-dotted curves), for representative core-shell $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ samples with 0-57% Ga content synthesized from 4.0 nm InP quantum dots. The exciton density of states and oscillator strengths from the theoretical calculations are shown as gray sticks below the x-axis and black sticks above the x-axis, respectively. For panels (A)-(E), the oscillator-strength sticks are plotted on the same y-scale to allow direct comparison of the composition-dependent changes in oscillator strength. (I) Photoluminescence excitation (PLE) spectra of the same samples, collected at the corresponding emission maxima and at half of the maximum emission intensity on the high-energy side; the inset illustrates this measurement schematically. (J) Comparison of the linewidths of the first excitonic feature in the ensemble absorption spectrum and the PLE spectrum of the representative $\text{In}_{0.86}\text{Ga}_{0.14}\text{P}/\text{ZnS}$ sample, with the PLE collected at the emission maximum. The linewidths are estimated from the full width at half maximum (FWHM) of Gaussian fits (shaded) to the low-energy flanks of the respective peaks. (K) Summary of the absorption and PLE linewidths extracted for the representative core-shell $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ samples shown in (A)-(D).

Calculated absorption spectra are consistent with the experimental observation that the sharpness of the excitonic features declines as gallium content increases. Importantly the theoretical observations are not convoluted with other sources of broadening, such as size distribution or composition distributions. Although ssNMR studies establish that the In and Ga atoms are randomly distributed at the cation sites of the ternary III-V lattice, particle-to-particle compositional variation remains a possible source of added heterogeneity in alloyed nanocrystals. We have previously established that ensemble diffraction techniques are insensitive to these subtle structural differences, but the emissive core-shell $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ nanocrystals allow us to explore this optically. Recording PL excitation (PLE) spectra allows us to selectively look at the spectral features of a smaller subpopulation instead of the entire ensemble. We, therefore, seek to compare the spectral heterogeneity of these alloyed nanocrystals using the corresponding absorption and PLE line widths for excitonic transitions. We can further quantify the PLE and ensemble absorption line widths using the full width at half-maximum (FWHM) of Gaussian fits to the low energy flanks of the respective peaks. Fig. 3.22J explains this analytic scheme for a representative sample $\text{In}_{0.86}\text{Ga}_{0.14}\text{P}/\text{ZnS}$; the results for these $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ samples are summarized in Fig. 3.22K. It is evident that each individual PLE spectrum becomes broader at higher gallium concentrations. Ensemble broadening from population ripening at elevated temperatures alone cannot explain the broadening of excitonic features in individual PLE spectra. Previous computational and experimental works have established that the energy states of homogeneously alloyed nanocrystals are not simple arithmetic means of their individual components. [261, 262] Instead, atomic disorder-related symmetry breaking can lead to the formation of additional mixed states, resulting in broadened spectral features during excitonic transitions, consistent with our observations. Furthermore, the theoretical model in this work incorporates the atomistic details and local strain effects through atomistic pseudopotentials, and thus, the “mixing of excitonic states” of the alloyed system is directly captured by our electronic structure calculations and can be observed from the density of states in Fig. 3.22A-H. Sample inhomogeneity is accounted for in the calculated absorption spectra through the energy-dependent Gaussian broadening and is kept the same across different Ga compositions. Therefore, the theoretical calculations in this work help conclude that exciton state mixing due to symmetry breaking is the main contributor to the broadened absorption features in $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs with high Ga composition. We probe this in more detail with transient absorption studies, and the results are summarized in a later section.

We estimate the PL decay lifetimes from time-resolved PL studies (Fig. 3.18E). Time-resolved photoluminescence (TRPL) of the $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ samples with varying sizes and Ga-to-In ratios does not show any fast early-time (sub-nanosecond) decay components usually associated with non-radiative recombination channels, which is typical for samples with high PL quantum yield. The faster radiative decay channel is the major contributor in each of these high-quality core-shell samples from a subsequent biexponential fit to the decay profile. A comparison of the TRPL decay profiles of these $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ samples in Fig. 3.18E illustrates a remarkable trend: the PL decay lifetime increases monotonically, while the PLQY decreases with increasing gallium content, which is difficult to explain by

a trapping mechanism. We estimate the radiative lifetime by combining the PL $1/e$ decay time constant and PLQY, providing us with an insight into the materials' intrinsic radiative lifetime (Fig. 3.18F). Importantly by directly measuring the radiative lifetimes, the trends we observe are independent of the quality of surface passivation during synthesis or other defects, which can lead to non-radiative recombination.

Radiative lifetimes at room temperature are calculated from the exciton energy and transition dipole moment for the calculated exciton states according to the equation

$$\tau_r = \frac{3\pi\epsilon_0\hbar c^3}{\omega^3|\boldsymbol{\mu}|^2}, \quad (3.31)$$

where c is the speed of light, and $\hbar\omega$ is the exciton energy. For the same gallium percentage, multiple configurations with random gallium distributions are considered, rendering the mean and standard deviation of the radiative lifetimes. As summarized in Fig. 3.18F, the trends are quite evident. An addition of up to $\sim 30\%$ Ga into the $\text{In}_{1-x}\text{Ga}_x\text{P}$ cores has only a minor effect on radiative lifetime and quantum yield, while a further increase of Ga content up to 60% is accompanied by a decline in PLQY down to 48% , along with a more than 3-fold increase in radiative lifetime, from 54 to 175 ns. The rate of radiative decay is inversely proportional to the calculated radiative lifetime, so we conclude that the oscillator strength of excitonic recombination in these systems is independent of composition when Ga content is below 35% and gradually decreases with increasing gallium content above 35% . Theoretical calculations in this work show good agreement with experimental measurements and demonstrate the same trend of decreasing absolute absorption intensity (Fig. 3.22A-H) and increased radiative lifetimes (Fig. 3.18F) as Ga concentration increases in alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs of the same size. A direct-gap-like excitonic transition characterized by a large oscillator strength would be from the Γ valley of the conduction band to the Γ valley of the valence band. In bulk crystals, the oscillator strength for the transitions from X or L valleys to Γ valley is significantly lower. We ascribe the diminishing oscillator strength of excitonic recombination in Ga-rich $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ QDs to an increased mixing of electron states originating from the X and Γ valleys. In bulk $\text{In}_{1-x}\text{Ga}_x\text{P}$ crystals, the direct-to-indirect transition is observed at $x \sim 0.75$ gallium content (Fig. 1.3), thus motivating exploration of quantum-confined samples with even higher gallium contents.

Transient Absorption (TA) Spectroscopy

We performed femtosecond transient absorption (TA) measurements on the $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ nanocrystals synthesized from 4.9 nm InP cores, which displayed absorption and PL characteristics of direct-gap-like behavior (38% Ga), intermediate behavior (65% Ga), and indirect-gap-like behavior (78% Ga), respectively. Measurements were performed using a 35 fs, 2 kHz Ti:sapphire laser with time-delayed white-light probe pulses produced in a 2 mm sapphire plate and 1 kHz pump pulses centered at 400 nm, generated by second-harmonic conversion of the fundamental. At these pump energies, the samples are excited well above the band gap of the $\text{In}_{1-x}\text{Ga}_x\text{P}$ core but below the absorption onset of the ZnS shell. All time-resolved

absorption spectra were collected at room temperature from stirred solutions, first at low excitation fluence such that only single-exciton dynamics were observed. Because the TA data were collected on ZnS-shelled samples, the measured dynamics more closely reflect intrinsic carrier relaxation than surface charge trapping. The similarity between the UV-vis absorption features of unshelled and shelled samples indicates that the shell has minimal impact on the band-edge absorption spectra, consistent with a type-I band alignment between the core and shell materials. The key observation is that a direct-gap semiconductor is expected to show both a ground-state bleach (GSB) signal and a photoinduced absorption (PIA) signal, whereas indirect-gap materials are expected to show only a PIA signal.

The transient absorption map for $\text{In}_{0.62}\text{Ga}_{0.38}\text{P}/\text{ZnS}$ nanocrystals shows a strong ground-state bleach signal (negative ΔA) centered at 605 nm, which develops within ~ 1 ps after the pump pulse and slowly decays over the nanosecond timescale of the measurement (Fig. 3.23C). The bleach signal corresponds well to the excitonic feature observed in the linear absorption spectrum of the sample. This behavior is consistent with a typical direct-band-gap semiconductor nanocrystal, in which the $1S_e$ - $1S_h$ excitonic transition is bleached once the photoexcited carrier cools to the band edge. A line cut of the TA signal at the maximum bleach amplitude shows a slow decay of the bleach signal, consistent with the timescales observed by TRPL (Fig. 3.23F). We also observe a PIA signal at wavelengths to the red of the bleach feature, which likely arises chiefly from excitation of conduction-band electrons by the probe pulse into near-continuum states above the band edge.

Next, we turn to the $\text{In}_{0.22}\text{Ga}_{0.78}\text{P}/\text{ZnS}$ sample (Fig. 3.23E,H), which showed a diffuse absorption onset and lacked detectable photoluminescence at room temperature or at 77 K. Here, we observe exclusively a PIA signal across the probed spectral range and do not detect any trace of a bleach feature. This behavior is consistent with that expected for an indirect-gap material, where the photoexcited electron and hole reside in different valleys of the conduction and valence bands; the momentum mismatch between them prevents the formation of an optical bleach signature. The PIA signals measured at 750 and 561 nm both form within 1 ps and slowly decay over the 1 ns measurement window.

We next discuss the TA dynamics of the $\text{In}_{0.35}\text{Ga}_{0.65}\text{P}/\text{ZnS}$ sample. This sample showed a diffuse absorption onset and weak PL at room temperature. Transient absorption reveals the formation of a bleach signal centered at 563 nm, which reaches its maximum amplitude at 800 fs. This bleach signal then decays rapidly within 20 ps, such that at later times only a PIA signal is observed across all wavelengths after ~ 30 ps (Fig. 3.23D,G). These carrier dynamics are notable because they are not simply a linear combination of the direct-like and indirect-like dynamics of the low- and high-gallium samples, respectively. One possible interpretation is that, after photoexcitation and carrier cooling, there is initially a population of carriers in direct Γ -like valleys as well as a second conduction-band state with X-like character and similar or slightly lower energy than the Γ -like valley. Intervalley scattering from the Γ -like valley to the X-like valley within ~ 20 ps efficiently removes carriers that can undergo direct transitions, causing the optical bleach signature to decay rapidly. Interestingly, the TRPL of the $\text{In}_{0.35}\text{Ga}_{0.65}\text{P}/\text{ZnS}$ sample shows an IRF-limited fast component together with an extremely long decay component, suggesting that scattering back into the direct channel at

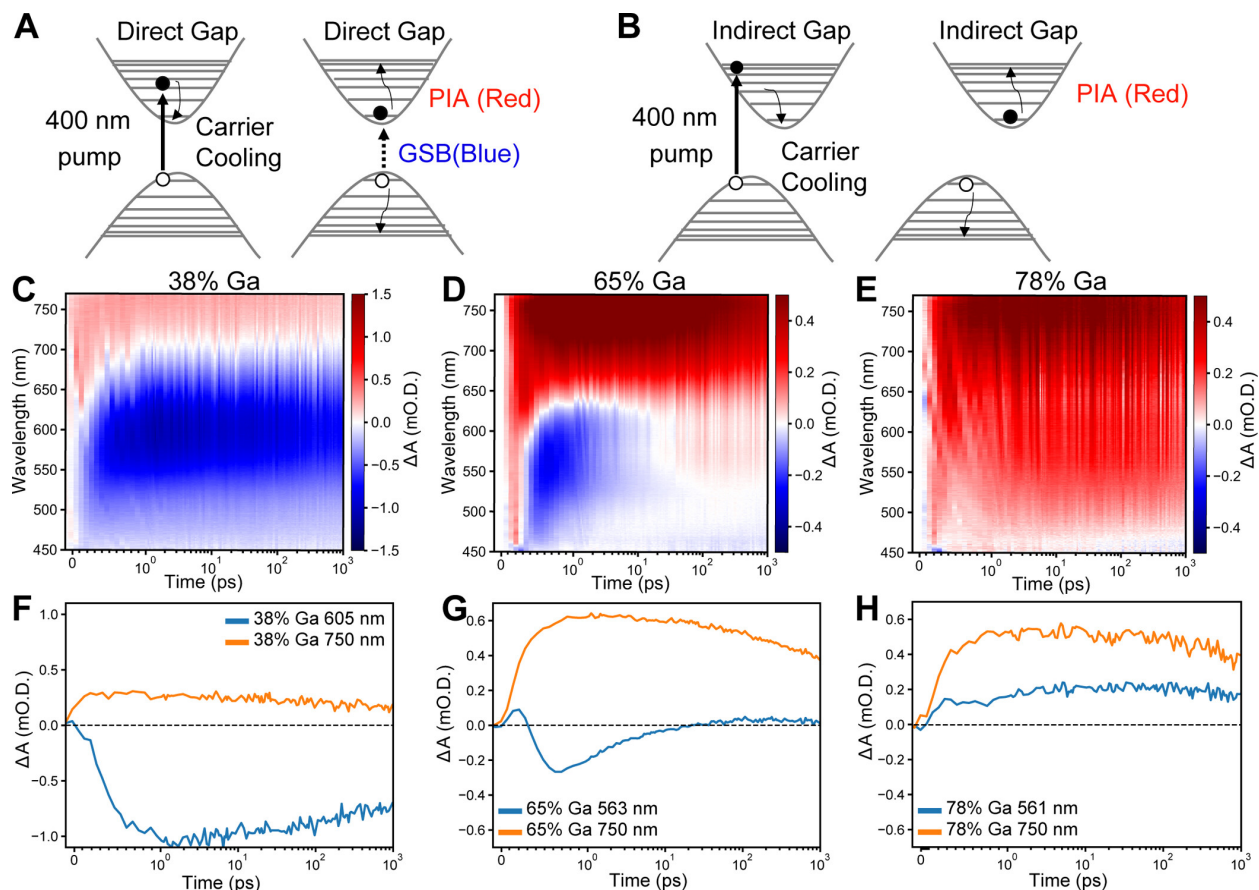


Figure 3.23: Schematic representation of the expected transient absorption signals for (A) a direct-band-gap semiconductor and (B) an indirect-band-gap semiconductor. GSB denotes ground-state bleach (negative ΔA), and PIA denotes photoinduced absorption (positive ΔA). Low-fluence transient absorption dynamics under 400 nm excitation are shown for In_{1-x}Ga_xP/ZnS quantum dots with gallium contents of (C) 38%, (D) 65%, and (E) 78%. Line cuts of the transient absorption signal at the maximum bleach amplitude, together with PIA traces at 750 nm, are shown for large In_{1-x}Ga_xP/ZnS nanocrystals with gallium contents of (F) 38%, (G) 65%, and (H) 78%.

late times can still give rise to PL. The existence of low-energy dark states and higher-energy bright states is consistent with the exciton manifold of the 65% Ga sample (Fig. 3.22E).

We also pumped the $\text{In}_{0.35}\text{Ga}_{0.65}\text{P}/\text{ZnS}$ sample directly into the lowest-energy states using a pulse centered at 640 nm and found that the decay of the optical bleach signature follows similar dynamics to those observed with 400 nm pumping. In this experiment, the sample is preferentially excited into band-edge states with relatively large oscillator strength. Since similar decay dynamics are observed even when starting from the band-edge state, we conclude that the carrier population transfer occurs directly from the direct-gap-like state to another optically inactive state. While the bleach signature decays on the ~ 20 ps timescale, the PIA signal remains relatively constant over the 1 ns measurement window, indicating that photoexcited carriers remain in the nanocrystal but with a momentum mismatch that prevents optical bleaching. Because of the lighter effective mass of the electron, the PIA signal is likely primarily sensitive to the electron population; thus, retention of the PIA signal despite rapid bleach decay is consistent with transfer of the electron population to X-like valleys. Taken together, these TA results are consistent with conversion of these QD emitters from direct-like to indirect-like band structures at $\sim 65\%$ gallium. Near the direct-to-indirect transition composition, the excited-state dynamics can become complicated by nearly isoenergetic states with different oscillator strengths.

Direct- and indirect-like electronic states in nanoconfined materials

The previously discussed transient absorption dynamics, TRPL, radiative rate, and molar extinction coefficient measurements indicate that the band-edge electronic state in $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ with $> 50\%$ Ga may contain states with indirect-gap-like character, which have a lower oscillator strength. They also motivate a broader question: how should direct and indirect gaps be defined in confined nano-materials? In bulk semiconductors, optical transitions must conserve both energy and crystal momentum, so the distinction between direct- and indirect-gap materials is set by the band extrema in momentum space. In nanocrystals, however, finite size breaks translational symmetry and relaxes momentum conservation, allowing mixing between states derived from different crystal momentum. As a result, the optical response need not follow a rigid bulk-like restriction, and it is more appropriate to describe nanocrystals in terms of direct-like and indirect-like behavior. $\text{In}_{1-x}\text{Ga}_x\text{P}$ provides an especially useful model system for this discussion because alloying continuously tunes the conduction-band-edge character from Γ -like to X-like, while quantum confinement modifies the extent to which these valley-derived states mix.

In bulk III-V semiconductors, the degeneracy of the conduction band Γ -valley is 2, the conduction band L valley is 8, and the conduction band X-valley is 6. In strongly quantum-confined semiconductors, the definition of direct vs indirect transitions becomes fuzzy owing to translational momentum relaxation. To understand this effect experimentally, we probe state filling in the $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ QDs synthesized from 4.0 nm InP cores using fluence-

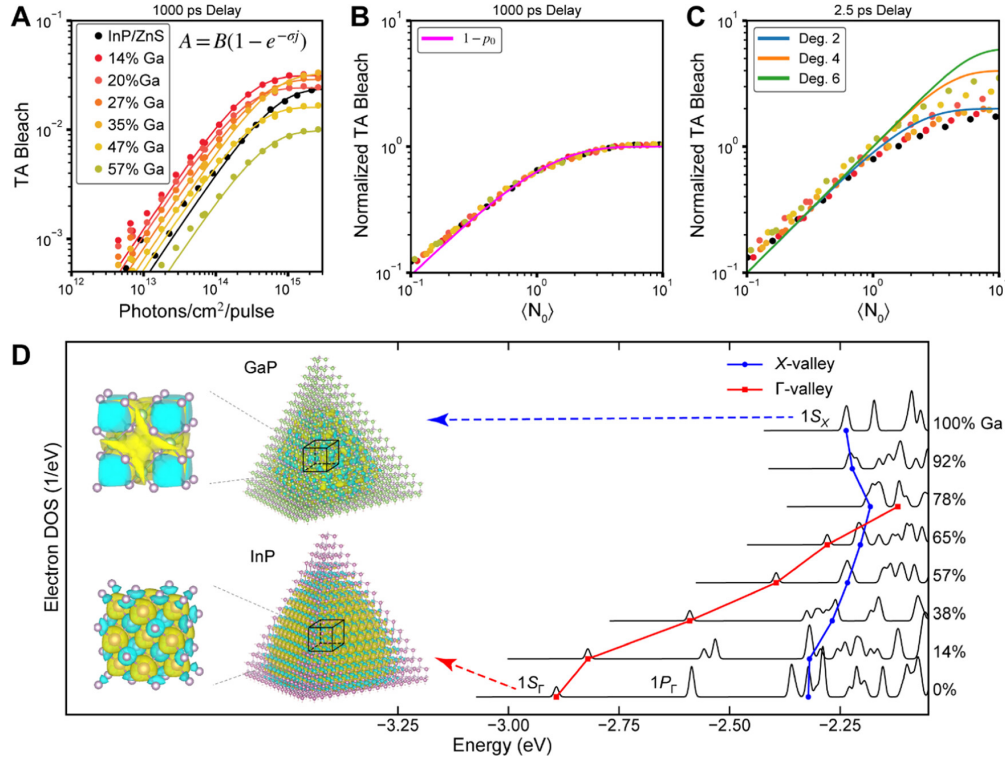


Figure 3.24: State filling in $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ nanocrystals with a 4.0 nm core diameter. (A) Bleach amplitude at a 1000 ps delay as a function of pump fluence (circles), together with fits based on single-exciton Poisson statistics used to extract the absorption cross section (σ) and bleach-amplitude scaling factor (B) for $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ nanocrystals with varying gallium contents. (B) Normalized transient absorption (TA) bleach signal at a 1000 ps delay as a function of the initial average excitation, $\langle N_0 \rangle$. The pink line shows the Poisson distribution describing the total number of singly photoexcited nanocrystals remaining after Auger recombination. (C) Normalized TA bleach signal at a 2.5 ps delay, before significant Auger recombination, as a function of the initial average excitation, $\langle N_0 \rangle$. The blue, orange, and green lines show model Poisson excitation statistics for ground-state bleach signals with degeneracies of 2, 4, and 6, respectively. (D) Density of states (DOS) of the conduction-band-edge electron states in alloyed quantum dots. The DOS for each gallium composition is vertically offset for clarity. The energies of the twofold-degenerate Γ -valley-like ($1S_\Gamma$, red squares) and sixfold-degenerate X-valley-like ($1S_X$, blue circles) conduction-band states are tracked as a function of gallium content. In the inset, the conduction-band-edge electron wavefunctions of tetrahedral InP and GaP quantum dots ($1S_\Gamma$ and $1S_X$, respectively) are shown. The Bloch wavefunctions are taken from the center of each quantum dot. Atom colors: pink, In; green, Ga; purple, P. Isosurface colors: yellow, positive; blue, negative.

dependent TA. We use the bleach signal for analysis, which reflects the population of the electron states due to the high degeneracy of the valence band and lighter effective mass of the electrons compared to the holes. [263] First, we determine the absorption cross-section, σ , and bleach amplitude scaling factor by fitting the power-dependent bleach signal at 1000 ps (after Auger recombination, ensuring that only single excitons remain in the QDs) according to the equation

$$A = B(1 - e^{-\sigma j}) \quad (3.32)$$

where A is the magnitude of the TA bleach signal, B is the bleach amplitude scaling factor, σ is the absorption cross-section per dot at the pump wavelength, and j is the pump laser fluence (Fig. 3.24A). [264] Fig. 3.24B shows that all samples fall on a universal curve for single excitations at long times, using σ and B determined from the fits. [260] In Fig. 3.24C, we use B and σ to measure the normalized bleach amplitude for the early-time signal at 2.5 ps (before significant contribution from Auger recombination). For $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ samples that have up to 35% Ga incorporated, we observe saturation at a normalized bleach signal of 2, consistent with a band-edge degeneracy of 2. This result is consistent with the behavior of a typical III-V direct-gap semiconductor. For samples with 47 and 57% gallium, we observe deviation of the fluence-dependent bleach signal from excitation statistics for a band-edge degeneracy of 2. Instead, the bleach amplitude continues to increase at high excitation densities before eventually becoming sublinear. The data for the 47-57% Ga samples approach the excitation statistics of 4. Thus, our data suggest that incorporating gallium into our samples alters the degeneracy of the band-edge state.

The evolution of band-edge state degeneracy as the gallium concentration is increased is further analyzed using atomistic pseudopotential calculations. [249] The main changes observed in bulk alloys were attributed to changes in the conduction band minima as the system transitions from InP to GaP. In NCs in the strong quantum confinement regime, one has to consider excitonic effects; however, since the calculated excitonic states near the onset of absorption comprise mainly a single quasi-electron state at any gallium composition, it is sufficient to analyze the quasi-electron structure as the content of Ga varies. Fig. 3.24D shows the results for $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs constructed from 4.0 nm InP NC. At 0% gallium (i.e., InP QD), the first several electron states are the 2-fold and 6-fold degenerate states with envelope function of 1S and 1P shapes, as expected from the effective mass approximation. [60] Meanwhile, at 100% gallium (i.e., GaP QD), the lowest electron states are 6-fold degenerate. These states in GaP also have spherical 1S envelope functions, but their Bloch wavefunctions (extracted from the center of the QD) have significantly different symmetry and spatial attributes (as shown in Fig. 3.24D insets). Specifically, in the tetrahedral InP QD, the lowest quasi-electron density is centered on each atom, while in the GaP QD, it is centered around the tetrahedral cavity formed by four neighboring P atoms. The two Bloch functions and their corresponding electron states are named “ Γ -valley” and “X-valley”, respectively.

Using the symmetry and spatial features of the Bloch wavefunctions, we identify and track the $1S_\Gamma$ and $1S_X$ electron states as gallium content increases. As shown in Fig. 3.24D, the energy of $1S_\Gamma$ electron states increases faster than $1S_X$, leading to a crossover of the Γ -valley-

like to X-valley-like band-edge electron state at 65-78% gallium content, in agreement with the experimental observations that the direct-to-indirect transition in $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs occur around $x = 65\text{-}78\%$ and helps decipher the atomistic details in its electronic structures. The electronic structure calculations allow us to better interpret the observed increase in state degeneracy measured by TA. Formally the calculations show that the lowest $1S_\Gamma$ state is 2-fold degenerate and the $1S_X$ state is 6-fold degenerate, not exactly the ~ 4 -fold degeneracy inferred by TA. We notice that as the gallium content in $\text{In}_{1-x}\text{Ga}_x\text{P}$ is increased, the splitting between the $1S_\Gamma$ and $1S_X$ electron states decreases. Both the $1S_\Gamma$ and $1S_X$ electron states give rise to the manifold of bright excitonic transitions observed in Fig. 3.22D. Due to the close spacing of the states, the bleach observed is actually measuring the state filling of the manifold of closely spaced states with mixed $1S_\Gamma$ and $1S_X$ characters. Thus, based on our measurements, in the 57% gallium sample, up to four excitons can reside near the band edge simultaneously. In support of this interpretation, we observe a redshift of the bleach feature from early time to late time, suggesting that as Auger removes the multicarrier population from higher energy states in the manifold, only the exciton in the lowest energy state remains.

Extension to GaPAs alloyed QDs with DeepPseudopot

Having established in $\text{In}_{1-x}\text{Ga}_x\text{P}$ that alloying can drive a crossover from direct-like to indirect-like band-edge behavior in nanocrystals, we next ask whether this is a more general feature of alloyed quantum dots. To address this question, we extend the analysis using DeepPseudopot, introduced in Chapter 2. DeepPseudopot generalizes the traditional atomistic semi-empirical pseudopotential framework to a machine-learned form while retaining its central advantage: an explicit atomistic description of quasiparticle states in nanostructures with arbitrary composition and geometry. We first verify that DeepPseudopot reproduces the same qualitative conclusions for $\text{In}_{1-x}\text{Ga}_x\text{P}$, thereby providing continuity with the earlier pseudopotential analysis. We then apply the same framework to $\text{GaP}_{1-x}\text{As}_x$ nanocrystals to test whether an analogous direct-to-indirect crossover emerges there as well. In this way, the $\text{In}_{1-x}\text{Ga}_x\text{P}$ case is elevated from a specific example to a broader framework for understanding alloy-driven valley crossover in confined semiconductor nanocrystals.

Motivated by recent experimental advances in the molten-salt synthesis of general alloyed III-V nanocrystals, we also tested the transferability of DeepPseudopot to ternary alloyed nanoscale systems. Geometries of $\text{In}_{1-x}\text{Ga}_x\text{P}$ and $\text{GaP}_{1-x}\text{As}_x$ nanocrystals were constructed through random ion exchange starting from pristine tetrahedral InP or GaP nanocrystals, respectively, in a manner that mirrors the experimentally motivated alloying pathway. [79] For each alloy composition, we generated three independent random alloy configurations. These two alloy systems were chosen because both involve GaP and therefore provide a useful platform for examining composition-driven direct-to-indirect band-gap transitions in the nanocrystal limit.

Using the DeepPseudopot model validated on binary III-V nanocrystals, we predicted the fundamental gaps of these ternary alloyed nanocrystals and compared them with the corresponding bulk alloy trends. Figure 3.25 shows the bulk direct-to-indirect crossover

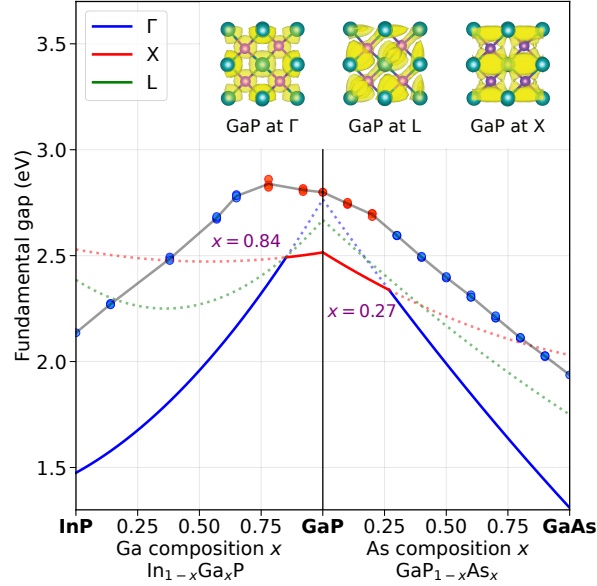


Figure 3.25: Fundamental band gaps of $\text{In}_{1-x}\text{Ga}_x\text{P}$ and $\text{GaP}_{1-x}\text{As}_x$ ternary alloys. Bulk alloy band gaps at the Γ , X , and L valleys (dotted lines) were interpolated using a simple quadratic form with experimental bowing parameters [265], with the lowest-energy branch at each composition highlighted by a solid line. The bulk direct-to-indirect crossover compositions are indicated in purple. Nanocrystal (NC) band gaps are shown as dots, colored according to the dominant GaP valley character (inset). The gray line denotes the average NC band gap over three random alloy configurations at each composition.

behavior obtained by quadratic interpolation of the Γ , X , and L valley gaps between the binary endpoints, including experimental bowing parameters to account for deviations from linearity. [265] The nanocrystal fundamental gaps are consistently larger than their bulk counterparts because of quantum confinement, but they retain a strongly nonlinear dependence on composition. In both $\text{In}_{1-x}\text{Ga}_x\text{P}$ and $\text{GaP}_{1-x}\text{As}_x$, changes in the slope of the nanocrystal gap track the bulk crossover regime, indicating that the underlying valley competition persists even in the confined limit.

To further interpret these trends, we analyzed the character of the conduction-band-minimum states by projecting the nanocrystal quasiparticle wavefunctions onto bulk GaP Bloch states at the Γ , X , and L valleys. Each nanocrystal CBM state was then classified according to its dominant valley character, as indicated by the color coding in Fig. 3.25. The evolution of this valley character closely follows the observed changes in the composition dependence of the fundamental gap, providing direct evidence that both $\text{In}_{1-x}\text{Ga}_x\text{P}$ and $\text{GaP}_{1-x}\text{As}_x$ nanocrystals undergo a crossover from Γ -like to X -like band-edge states as alloy composition is varied. Thus, even though translational symmetry is broken and crystal

momentum is no longer a rigorous quantum number in nanocrystals, the language of direct-like and indirect-like behavior remains physically meaningful when interpreted through the valley-derived character of the band-edge states.

3.4 Conclusions and outlook

This chapter developed and validated an atomistic theoretical framework for understanding the excited-state photophysics of colloidal III-V nanocrystals, and connected this framework directly to a novel family of experimentally accessible III-V semiconductor nanomaterials. Recent advances in molten-salt synthesis have made high-quality gallium-containing III-V nanocrystals available with sufficient structural and optical quality for quantitative comparison with theory. In this context, atomistic excited-state modeling is not simply descriptive, but can provide a route to interpret measured optical observables, identify the microscopic origin of spectral features, and clarify how quantum confinement, shape, composition, and exciton-phonon coupling together determine nanocrystal photophysics.

For binary III-V nanocrystals, GaAs has emerged as a particularly effective platform for establishing this connection between theory and experiment. Within the DeepPseudopot framework, we computed **optical gaps**, **radiative lifetimes**, **Stokes shifts**, and **excitonic fine structure**, and showed that these quantities are consistent with measured ensemble optical properties. We then extended the analysis to **phonon-resolved photoluminescence** by developing an atomistic linear-response framework for single-nanocrystal emission based on exciton energies, phonon modes, and exciton-phonon couplings. After validating this approach against temperature-dependent single-nanocrystal spectroscopy in CdSe/CdS as a benchmark system, we applied it to GaAs nanocrystals to interpret fluorescence line narrowing and photoluminescence excitation measurements in terms of their underlying excitonic and vibronic structure. Together, these results show that atomistic modeling can quantitatively connect microscopic exciton-phonon coupling to experimentally observed emission line shapes in quantum-confined III-V nanocrystals.

For alloyed III-V nanocrystals, this chapter identified $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ quantum dots as a composition-controlled model system for studying the direct-to-indirect crossover under quantum confinement. The combined **transient absorption**, **time-resolved photoluminescence**, **radiative-rate**, and **absorption** measurements show that increasing gallium content progressively reduces oscillator strength and ultimately drives a transition from direct-like to indirect-like optical behavior. Atomistic pseudopotential calculations rationalize this crossover through the evolution of the conduction-band-edge character from Γ -like to X -like states. Fluence-dependent transient absorption further reveals that, near the crossover, the band edge is more accurately described as a closely spaced manifold of mixed valley-derived states rather than a single isolated level. More broadly, these results show that in confined nanocrystals, the distinction between direct and indirect semiconductors remains meaningful when interpreted through the **wavefunction atomistic character**, **degeneracy**, and **oscillator strength** of the band-edge states. Extending the same framework to

$\text{GaP}_{1-x}\text{As}_x$ suggests that this alloy-driven valley crossover is not unique to $\text{In}_{1-x}\text{Ga}_x\text{P}$, but reflects a more general design principle for composition-tunable III-V nanocrystals.

Taken together, the results of this chapter show how advances in synthesis and advances in atomistic theory can reinforce one another to enable predictive photophysics in semiconductor nanocrystals. The molten-salt synthetic platform provides access to previously unavailable, high-quality III-V materials, while the DeepPseudopot framework provides the electronic and vibronic resolution needed to interpret their excited-state behavior at the microscopic level. Looking forward, an important theoretical direction is the incorporation of higher-order exciton-phonon coupling and non-Condon effects into the spectral modeling framework. On the materials side, it will be especially important to test the generality of these conclusions in more complex nanocrystal architectures, including core-shell structures, ligand-modified surfaces, and broader III-V alloy families. More generally, the combination of composition control, atomistic electronic-structure analysis, and predictive optical modeling developed here establishes a foundation for the rational, computation-driven design of colloidal III-V nanocrystals with tailored radiative rates, spectral line shapes, thermal stability, and band-edge character for future photonic and optoelectronic applications.

Chapter 4

Phonon-assisted exciton relaxation dynamics in III-V alloyed nanocrystals

This chapter is adapted with permission from Beiye C. Li, Kailai Lin, Ping-Jui E. Wu, et al. **“Exciton-phonon coupling and phonon-assisted exciton relaxation dynamics in $\text{In}_{1-x}\text{Ga}_x\text{P}$ quantum dots,”** *Nature Communications* 16, 4424 (2025). [266] This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 International License.

In the previous chapter, we examined the static excitonic and optical properties of III-V semiconductor nanocrystals, including optical gaps, radiative lifetimes, Stokes shifts, exciton fine structure, and phonon-resolved single-nanocrystal photoluminescence. We showed that composition introduces an additional degree of freedom beyond quantum confinement, enabling the band structure, state ordering, and optical transitions of alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ nanocrystals to be tuned continuously through the direct-to-indirect gap crossover.

Having established how size and composition shape the excitonic spectrum, we now turn to the dynamical processes that follow photoexcitation. As discussed in Chapter 1, the relaxation of hot excitons in quantum dots is governed by the interplay between the excitonic level structure and exciton-phonon coupling, and alloying modifies both: it changes the density and character of excitonic states as well as the nature of their coupling to lattice vibrations. In binary quantum dots, the conventional bright-dark three-level model captures the temperature dependence of photoluminescence lifetimes, but it oversimplifies the exciton fine structure. [111–113] In alloyed systems such as $\text{In}_{1-x}\text{Ga}_x\text{P}$, compositional disorder lifts level degeneracies and produces a denser excitonic manifold, [79, 114] leading to qualitatively different relaxation pathways that require investigation beyond what binary models can provide. Composition and quantum confinement thus act as two complementary knobs for tuning not only static excitation energies but also the timescales and mechanisms of excited-state relaxation.

In this chapter, we investigate the influence of alloy composition on exciton level structures, exciton-phonon coupling, and femtosecond exciton relaxation dynamics in $\text{In}_{0.62}\text{Ga}_{0.38}\text{P}/\text{ZnS}$ (38% Ga) and $\text{In}_{0.35}\text{Ga}_{0.65}\text{P}/\text{ZnS}$ (65% Ga) QDs using coherent 2DES measurements and atomistic theoretical calculations. We describe the exciton level structure by integrating an atomistic semi-empirical pseudopotential model with the Bethe-Salpeter equation (BSE). Inspired by the unusual direct-vs-indirect gap transition across the two compositions of $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs, we map QD exciton densities onto the bulk Bloch wavefunctions and quantify the “quasi-momentum” of high-energy QD excitons. We calculate excitonic state-specific EXPC, decouple contributions from optical and acoustic phonon modes, and find that direct-gap QD excitons couple more strongly to optical phonons than indirect-gap excitons. Optical phonons and their EXPC are also measured using Raman spectroscopy with resonant excitations. [122, 123] Raman analysis and pseudopotential calculations show excellent agreement on longitudinal optical (LO) phonon Huang-Rhys factors, with similar values for 38% and 65% Ga QDs. Hot exciton relaxation dynamics, extracted from 2DES data and polaron-transformed Redfield calculations, show faster relaxation in 65% Ga QDs compared to 38% Ga QDs, with qualitative agreement between theory and experiment. We pinpoint the interplay between exciton level structure and EXPC as the key factor influencing both the timescale of this process and the energy-retaining states that slow charge carrier relaxation in 38% Ga QDs. These findings demonstrate that, beyond bandgap engineering, alloying intricately tunes nonradiative exciton dynamics and EXPC in III-V QD systems through energy-level structure, which can be precisely predicted by electronic structure calculations and dynamics simulations.

4.1 Steady-state characterization and modeling

Samples of $\text{In}_{0.62}\text{Ga}_{0.38}\text{P}/\text{ZnS}$ and $\text{In}_{0.35}\text{Ga}_{0.65}\text{P}/\text{ZnS}$ QDs with the same core size (4.92 nm) were chosen to avoid size-dependent excited state dynamics and EXPC. [104] In and Ga cations were alloyed uniformly, as validated by solid-state nuclear magnetic resonance and computational modeling. As shown in Fig. 4.1, both samples feature a broad excitonic transition in the ensemble steady-state absorption spectra. Emission peaks are at 1.88 and 1.96 eV for 38% Ga and 65% Ga QDs, respectively, where the blue shift is a result of bandgap widening with increasing Ga concentration. The broad exciton features observed in the experimental spectra were attributed to the size, shape and symmetry inhomogeneity of the QD ensemble.

Theoretical calculations reveal the detailed exciton level structures in the alloyed QDs. Exciton states were calculated using the atomistic semi-empirical pseudopotential method combined with the BSE to account for electron-hole correlation. [79, 135, 150, 158] The atomistic pseudopotentials were fitted to accurately reproduce ab initio bulk band structures and deformation potentials. We omitted modeling of the wide bandgap ZnS shell to reduce computational cost. The stochastic filter diagonalization method was used to selectively obtain the electron and hole states near the band edge with high accuracy and at reduced compu-

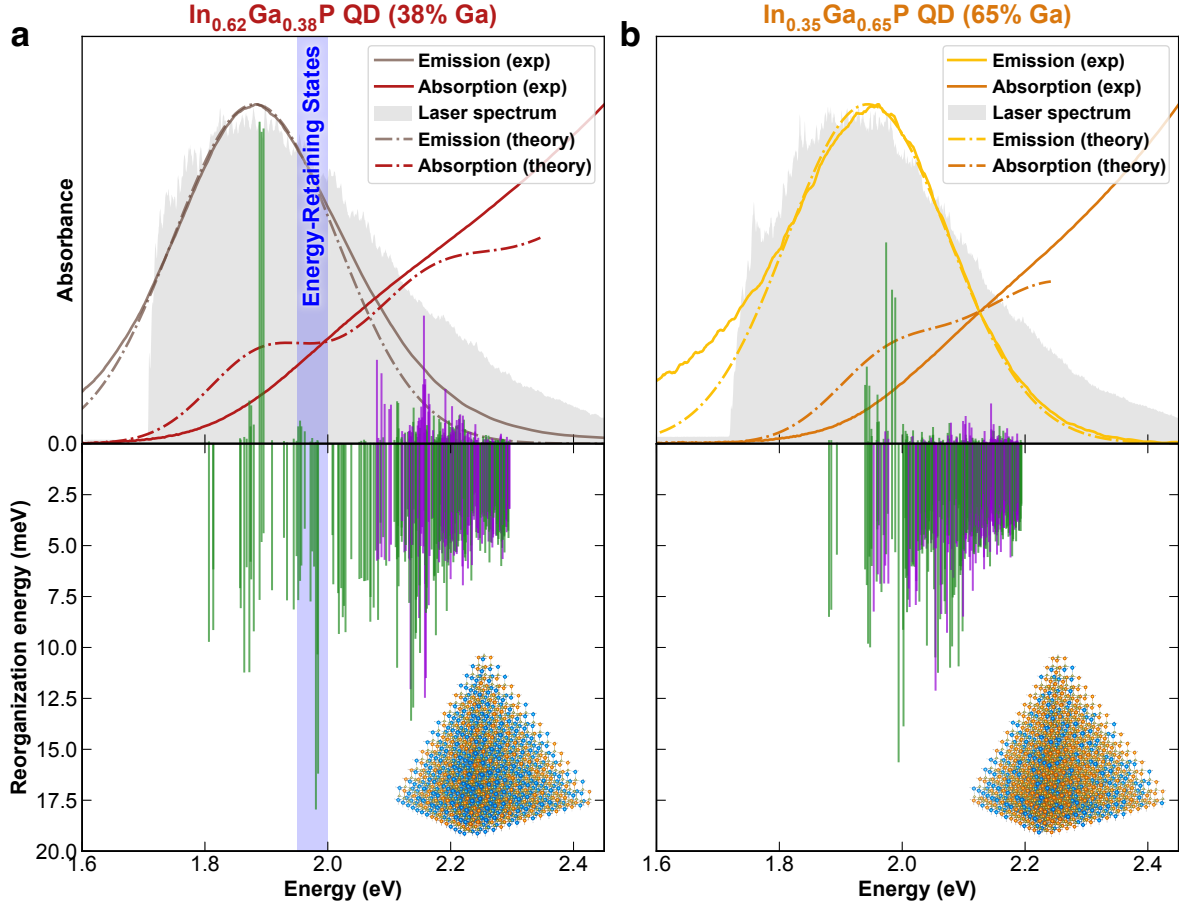


Figure 4.1: Optical spectra and phonon reorganization energies for In_{1-x}Ga_xP QDs. Absorption and emission spectra of **a** 38% Ga and **b** 65% Ga quantum dots (QDs) from experiments (solid lines) and theory (dashed lines) are shown. In the top panels, the exciton states are represented as bars with height corresponding to oscillator strength (OS). Exciton states labeled in green are assigned as “direct-like”, while states labeled in purple are assigned as “indirect-like”. Shaded gray region is the white light spectra used in the two-dimensional electronic spectroscopy (2DES) measurements. Shaded blue box in (a) highlights the ‘energy-retaining’ states in 38% Ga with high phonon reorganization energy. Bottom panel shows the phonon reorganization energy of exciton states in bar representation. Atom colors: blue—In, orange—Ga, olive green—P.

tational cost. [188] Oscillator strengths were calculated from the transition dipole moment between the ground and exciton wavefunctions, and are shown as the height of the colored bars above the energy axis in Fig. 4.1. More details on the semi-empirical pseudopotential

method, the equilibrium QD configurations, and BSE and oscillator strength calculations can be found in Chapter 3.2. Motivated by the composition-driven direct-to-indirect gap transition in alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs, we evaluated the “majority representation” coefficients of exciton states by projecting the QD wavefunction onto the Bloch wavefunctions of bulk GaP at the direct (Γ) and indirect (X , L) valleys (see Fig. 4.2 for details). [247, 267] We classify each exciton transition as either “direct-like” or “indirect-like” (green and purple in Fig. 4.1), disentangling their different contributions to exciton structure and EXPC.

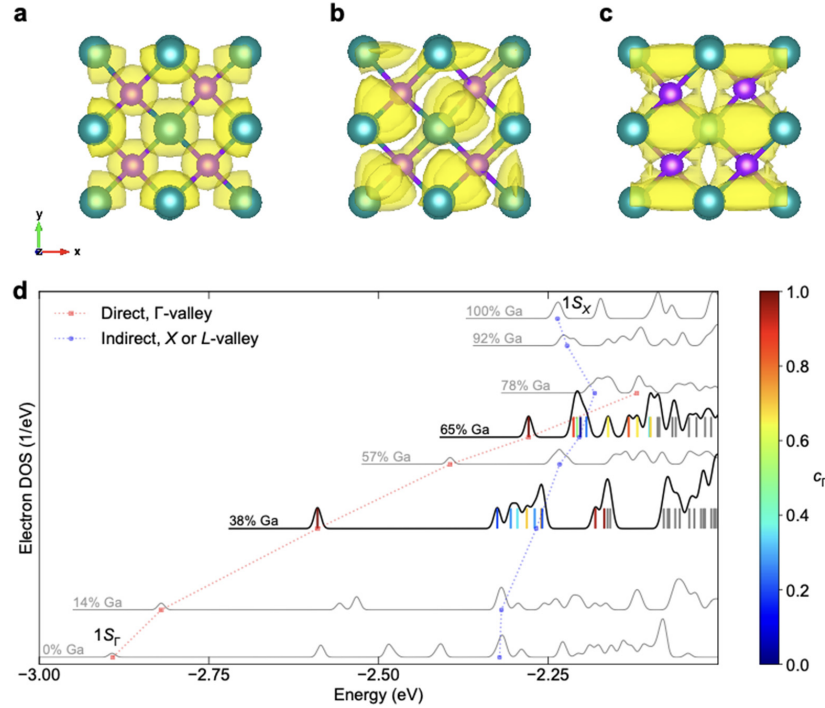


Figure 4.2: The density of the lattice periodic part of the Bloch wavefunction for the conduction band minimum of GaP at Γ (a), L (b), and X points (c) respectively. Colors: density isosurfaces – yellow, Gallium atoms – teal, Phosphorus atoms – purple. (d) The density of states of electron states for different alloy composition in $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs. The evolution of the direct-gap and indirect-gap electrons are shown in dotted lines. For 38% and 65% Ga QDs, the Γ -coefficients in the majority representation of the first ten electron states are shown according to the color bar.

Absorption and emission spectra were calculated from exciton energies, OS, and phonon reorganization energy (discussed below), and agreed well with the absorption onset energies and emission peak energies of the measured spectra. The broad exciton features observed experimentally are attributed to the presence of multiple bright states near the band edge, with more energetically dispersed bright states in 65% Ga QDs compared to 38% Ga QDs.

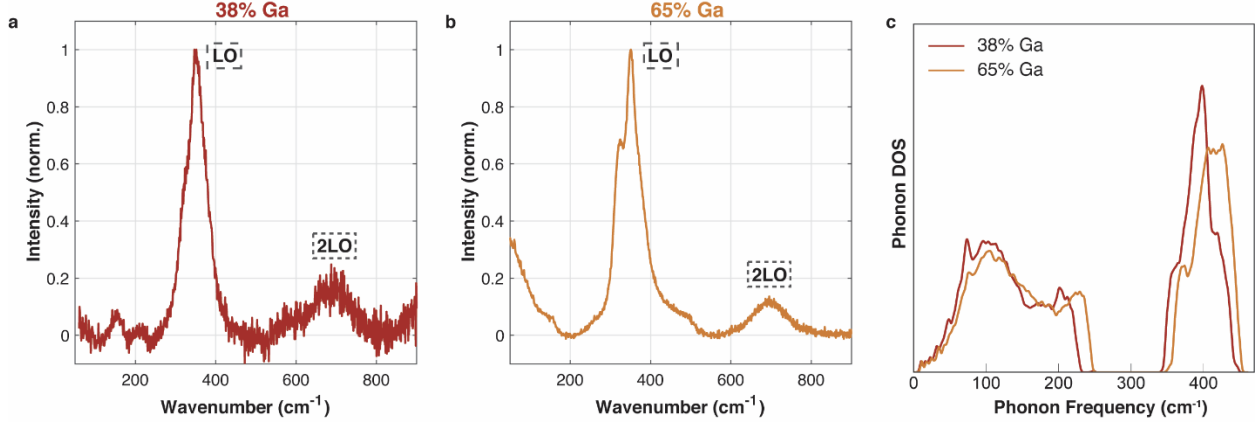


Figure 4.3: Resonant Raman spectra of 38% (a) and 65% Ga (b) In_xGa_{1-x}P QDs. LO and 2LO phonon peaks are identified. (c) The calculated phonon density of states for 38% and 65% Ga In_xGa_{1-x}P QDs using the classical Tersoff force field.

Inhomogeneity of QD ensembles in terms of size, shape, and crystal symmetry could also contribute to this broad exciton feature. [116] Both QDs exhibit bright direct-like excitons at the band edge, while 38% Ga QDs have larger overall OS, in agreement with previous work on composition-driven transitions in In_{1-x}Ga_xP alloyed QDs. In addition, both compositions have clustered indirect gap-like exciton peaks at higher energies with smaller OS. The energy separation between direct gap-like and indirect gap-like excitons is smaller for 65% Ga QDs due to their density of exciton states. This result is consistent with Vegard's law on the interpolation of conduction band minimum energy according to Ga content.

Phonons and their coupling to electronic states were characterized by Raman spectroscopy with resonant excitations (Fig. 4.3), where the optical phonons were resolved. For 38% Ga QDs, the peak of highest intensity at 347 cm⁻¹ is assigned as the LO phonon mode, with the second overtone peak experimentally resolved. We extracted the peak area by fitting each with a sum of Gaussian functions and calculated an experimental Huang-Rhys factor of 0.30 using the peak area ratio. This factor is a measurement of EXPC assuming a displaced harmonic oscillator model, which provides a numerical strength of overall electronic transition coupling to the LO phonons, complementary to theoretical spectral density analysis. [193, 268] The LO phonon for 65% Ga QDs is at 350 cm⁻¹ and, due to higher Ga concentration, vibrates at a higher frequency than that for 38% Ga QDs. The experimental Huang-Rhys factor is calculated as 0.29, similar to that of 38% Ga QDs. The Huang-Rhys factors for LO phonons were also calculated from the atomistic theoretical modeling (0.25 for 38% Ga, 0.34 for 65% Ga), and agree well with experiments. The similar EXPC strength obtained from both modeling and Raman spectroscopy suggests that EXPC is not the main factor contributing to the decrease of quantum yield with increasing Ga content (reported in the previous study). Rather, the inevitable introduction of indirect gap-like transitions

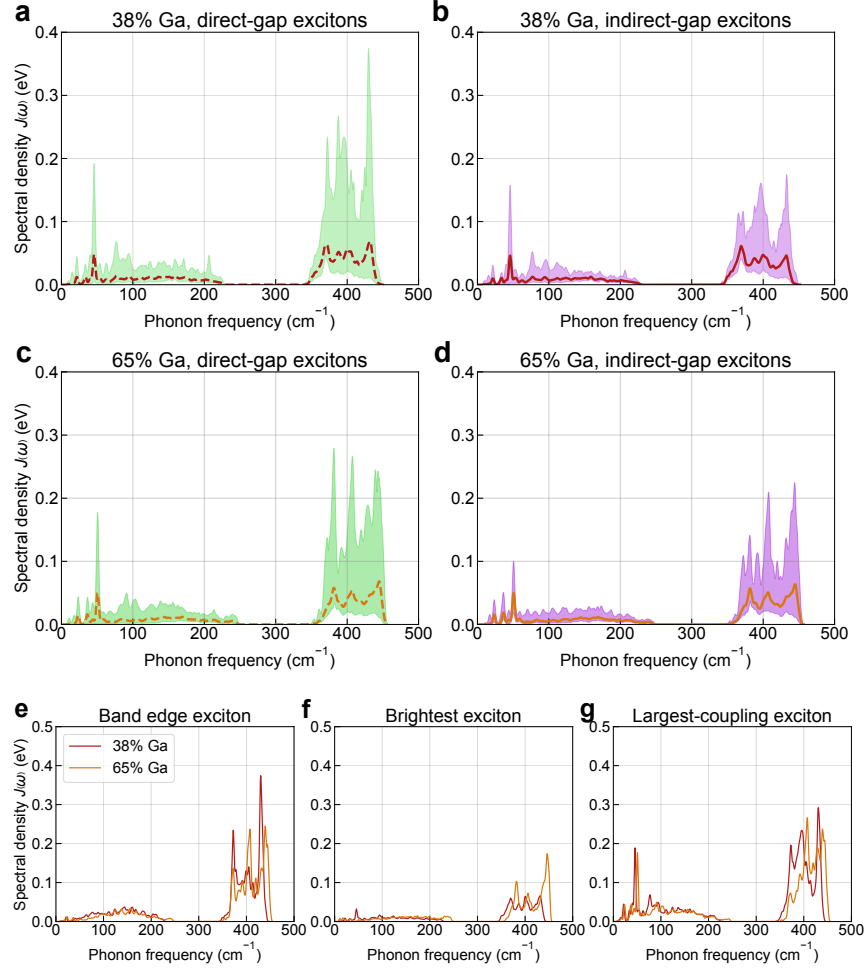


Figure 4.4: Spectral densities for direct-gap (dashed lines, green) and indirect-gap excitons (solid lines, purple) in 38% (a, b) and 65% Ga (c, d) QDs. The average spectral densities of all computed excitons are shown as red or orange lines. The color shaded areas represent the range of the spectral densities. Panels (e-g) compare the spectral densities between 38% (red lines) and 65% Ga (orange lines) QDs, for the band-edge exciton, the brightest exciton and the exciton with the largest exciton-phonon coupling.

due to Ga incorporation is more detrimental to the quantum yield.

Theoretically calculated phonon mode frequencies and EXPC were in excellent agreement with the Raman results. We used a previously parametrized Tersoff-type force field to relax the QD geometries and obtain normal modes from the mass-weighted Hessian matrix. [187] EXPC were calculated directly from the semi-empirical pseudopotential model with phonon modes obtained from the classical force field. Our model was parametrized based on the

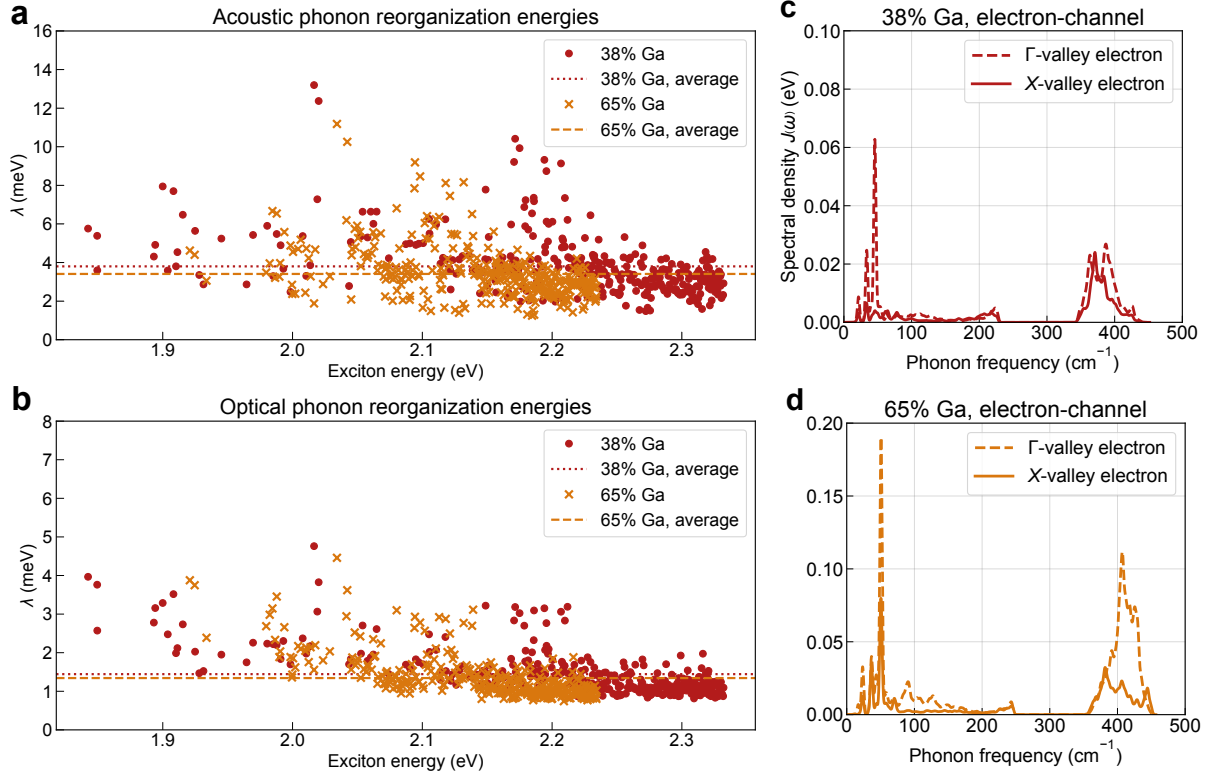


Figure 4.5: Acoustic (a) and optical (b) phonon reorganization energies for 38% and 65% Ga QDs. Electron-channel coupling is shown for the 38% Ga QD (c) and the 65% Ga QD (d), with Γ -valley electrons (direct; dashed lines) and X- or L-valley electrons (indirect; solid lines).

bulk deformation potentials and does not explicitly account for Fröhlich and piezoelectric coupling mechanisms. We are working on including long-range Coulomb components in our pseudopotential model to more accurately capture the Fröhlich-type interactions in III-V semiconductors. [128] The vibrational density of states for both 38% and 65% Ga QDs shows a clear ‘phonon gap’ at around 250-350 cm⁻¹, separating the acoustic and optical phonon branches, as expected from the phonon dispersion relations of bulk InP and GaP. [269] The calculated LO phonon frequencies of 65% Ga QDs are slightly higher than the 38% Ga LO phonon frequency, which is consistent with the assignment of the experimental Raman peaks. The calculated EXPC elements agree qualitatively with the experimentally extracted Huang-Rhys factors for the LO phonons and provide more elaborate details on the diagonal and off-diagonal (inter-exciton) couplings (see Fig. 4.1). The reorganization energies, which quantify the energy associated with lattice rearrangement upon vertical excitation from the ground state to a specific exciton state, are calculated for both QDs and plotted on the

bottom panels of Fig. 4.1. Overall, 38% and 65% Ga QDs have similar reorganization energies (see Fig. 4.4). Acoustic phonon contributions to the reorganization energy outweigh optical mode contributions due to their low frequency. Electron channel coupling is larger for indirect gap-like states; however, as hole channel coupling dominates the total EXPC, there is no significant difference in reorganization energies between direct-like and indirect-like exciton states (see Fig. 4.5). [127, 193, 270] Optical phonon couplings are noticeably smaller for indirect gap-like excitons, while the acoustic phonon couplings are similar for indirect-like and direct-like excitons, which is consistent with the k -dependence of EXPC in bulk polar semiconductors. In 38% Ga QDs, the excitonic states between $1S_h$ - $1S_e$ (around 1.8-1.95 eV) and $1P_h$ - $1P_e$ (around 2.05-2.3 eV) states exhibit larger reorganization energy, while similar states with large EXPC are absent in 65% Ga QDs (Fig. 4.1). The calculated EXPC for each exciton-phonon pair, along with the exciton level structure and reciprocal space decomposition, provides a clear picture of how electron-phonon coupling in bulk materials translates to confined alloyed nano-systems.

4.2 2DE spectra

The femtosecond excited state dynamics of 38% and 65% Ga QDs were measured using 2DES at room temperature under the single-photon excitation regime. Details of the home-built 2DES apparatus can be found in Ref. [271]. The broadband excitation is compressed to provide a near transform-limited pulse duration of 7.3 fs, which enables detection of ultrafast exciton relaxation in QDs. The time separation between two excitation pulses gives rise to an additional excitation energy axis, which yields a frequency-frequency correlation map at each waiting time. [272–274] The simultaneous excitation of all exciton states within the excitation range also leads to various coherent phenomena within the excited states. [100, 275] The time evolution of 2DE spectra for 38% and 65% Ga QDs within the first 1 ps upon photoexcitation is shown in Fig. 4.6. After the initial transient grating response, signals for both 38% and 65% Ga QDs form within the first 100 fs, with minimal spectral shift observed after signal formation is complete. The 2DE line shape of an elongated oval along the diagonal is a result of multiple excitonic levels with close energy spacing, and the presence of electronic inhomogeneity, giving rise to an energetically broad ground state bleaching (GSB) signal along the diagonal of 2DE spectra. [116, 126, 276–279] The off-diagonal width is influenced by the homogeneous linewidth of excitonic states and their couplings. At 48 fs, multiple peaks are observed for both samples along the diagonal with off-diagonal peaks indicating the couplings. These peaks may correspond to the increased number of bright states related to the exciton fine structure, which has also been observed in InP/ZnS [280] and CdSe QDs, [68] although scatter in the coherence time domain complicates the assignment. These peaks later broaden and evolve into a single broad peak on the 2DE spectra. This spectral lineshape, which is different from that of CdSe QDs, [120, 126, 277–279] is due to the overlap of off-diagonal peaks, indicating exciton state-state coupling, among closely spaced exciton levels. [116]

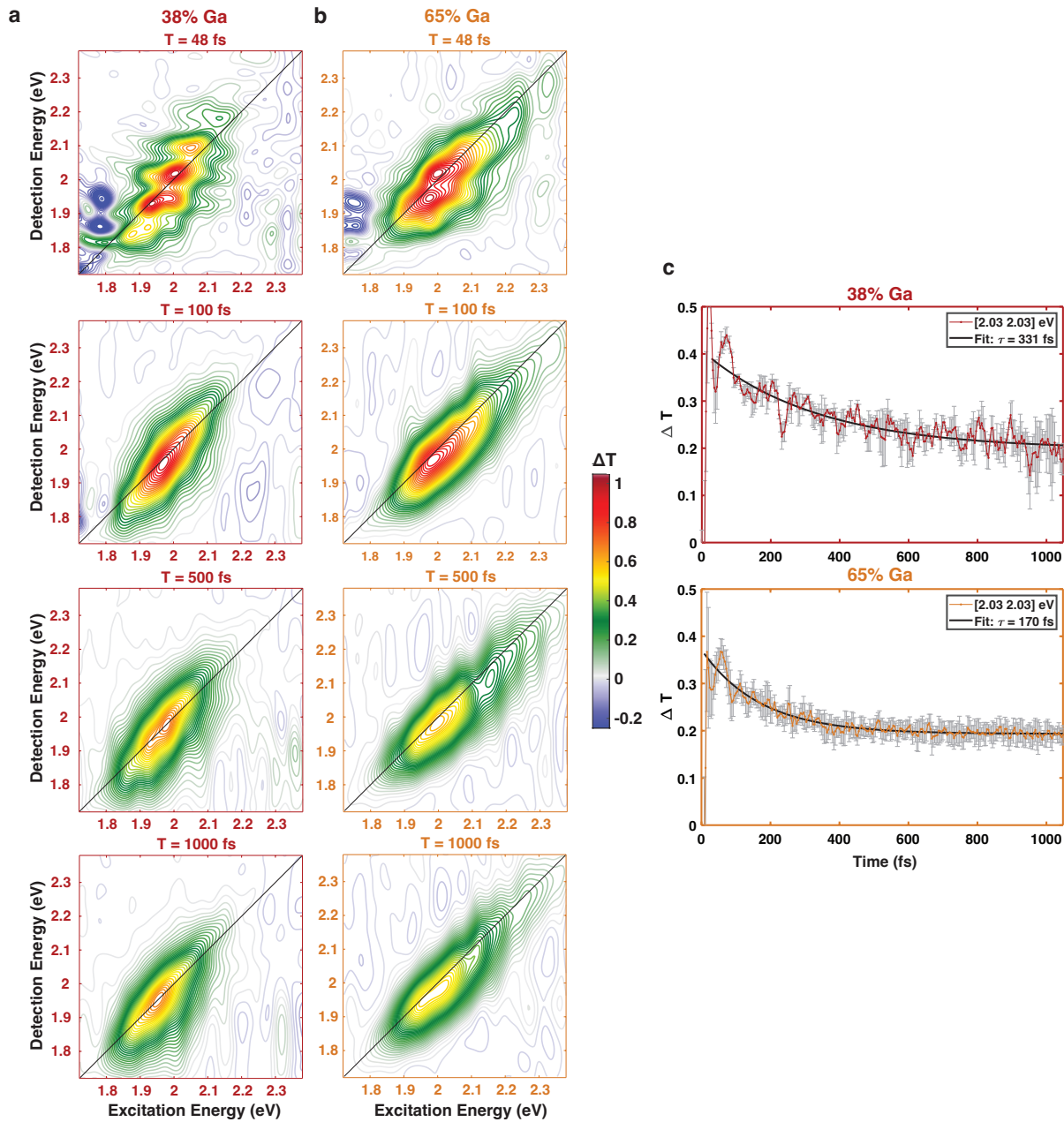


Figure 4.6: 2DE spectra and diagonal time traces of 38% and 65% Ga QDs. Absorptive 2DE spectra (normalized with respect to each data cube) at waiting times 48, 100, 500, and 1000 fs for **a** 38% Ga QDs and **b** 65% Ga QDs. **c** Diagonal decay of the absorptive signal at [2.03 2.03] eV for (top) 38% Ga and (bottom) 65% Ga QDs. Both decays are fit with single exponential function to extract the time constant for hot exciton cooling process.

A significant difference in the early-time 2DE spectra of 38% and 65% Ga QDs is observed at 500 fs, where the upper part of the 65% Ga QD signal (excitation and detection energies are above 2.08 eV) has a smaller signal amplitude than the lower region of the signal. We exclude the possibility of fast population dynamics by comparing the time evolution of the signal at two excitation energies, which shows a marginally faster decay component at early timepoints. This fast decay is later assigned as non-radiative exciton cooling (elaborated upon in the next section), and its overall timescale is extracted through singular value decomposition (SVD) analysis. Therefore, the lower signal amplitude is due to the lower oscillator strength of exciton states at this energy range, as also shown in the computed exciton level structures. Previous picosecond TA measurements of this composition reported a transition from GSB to excited state absorption at around 30 ps at the same spectral location as this low oscillator strength region, a transition which we also observe in the 2DES and TA picosecond dynamics of the current work. In 38% Ga QDs, the oscillator strength of indirect-like and direct-like exciton states are more comparable, which leads to relatively homogenous features in their 2DE spectra.

4.3 Exciton cooling dynamics

The fast exciton dephasing and non-radiative relaxation channels require further mechanistic investigation. Therefore, we calculated the phonon-mediated hot exciton cooling dynamics at the same energy range as the 2DE signals shown in Fig. 4.6. We obtained the EXPC matrix elements from the theoretical model and simulated the multi-phonon mediated hot carrier cooling dynamics using the polaron-transformed Redfield equation. [125] Our model focuses on the population dynamics (diagonal elements of the density matrix) and does not include coherent dynamics (off-diagonal elements). For the population dynamics simulation, a unitary polaron transformation is employed, which helps to rescale the coupling between phonon modes and excitonic state, and allows for the description of multi-phonon relaxation in the lowest-order perturbation theory. Such a multi-phonon relaxation process is central in describing the ultrafast dynamics of hot excitons, which has been discussed in previous work. [124] The excitonic states after transformation are dressed by the reorganization energy, and the transformed/rescaled exciton-phonon coupling is weaker. After polaron transformation, the equation of motion for the reduced density matrix representing the Hilbert space of the excitonic states is given by the non-Markovian time-local secular Redfield equations. The excitation energies (initial states) were chosen as 0.25-0.3 eV above the band edge exciton to match the energy range of 2DE signals.

Time traces of the total energy loss to phonons for 38% and 65% Ga QDs are plotted in Fig. 4.7a, b. The 38% Ga QDs show slower exciton cooling (245 fs) than 65% Ga QDs (91 fs), which is consistent with SVD analysis of 2DE dynamics. In the SVD analysis, the secondary principal component corresponds to dephasing and exciton cooling processes, and the associated time constants are 421 and 189 fs for 38% and 65% Ga QDs, respectively. The population dynamics and lifetimes of each energy window of excitons (Fig. 4.7e, f) match

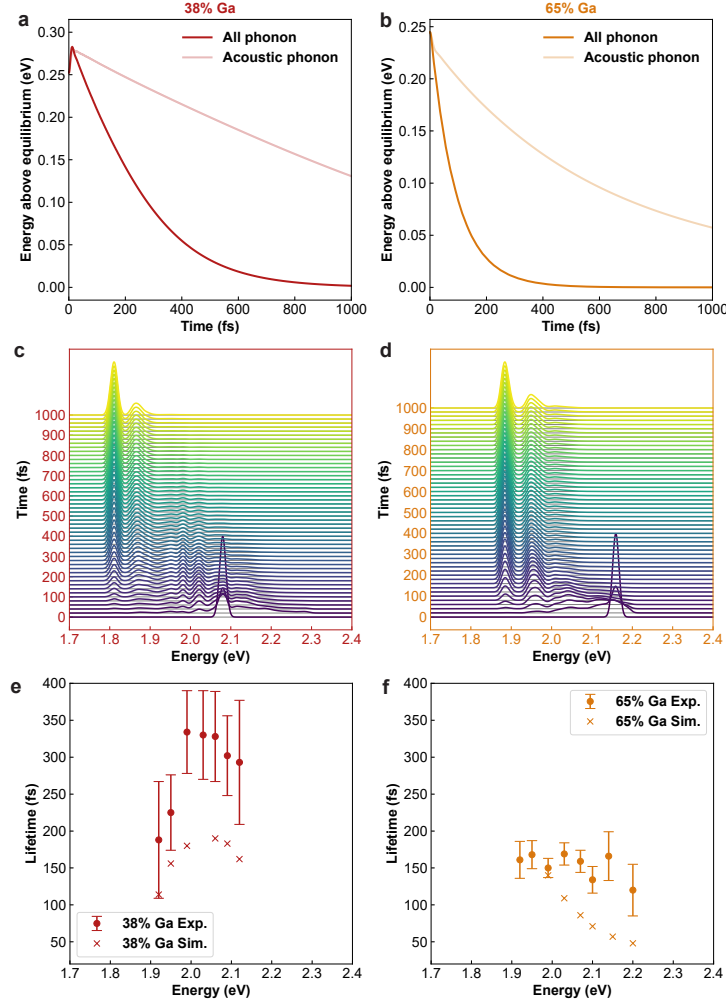


Figure 4.7: Simulated exciton cooling dynamics of 38% Ga and 65% Ga QDs. **a, b** Overall energy loss upon initial excitation with all phonons considered as compared to acoustic modes only. 38% Ga QDs show an overall energy loss time of 245 fs with all phonons considered in the calculation, and this time constant increases to 1936 fs when only acoustic phonon modes are considered. 65% Ga QDs show a faster energy loss time of 91 fs with all phonon modes considered, and this time constant decreases to 580 fs when only acoustic phonon modes are considered. **c** and **d** The calculated excitonic density of states over 1000 fs show population dynamics of **(c)** 38% Ga QDs excited at 2.12 eV and **(d)** 65% Ga QDs excited at 2.20 eV. **e** and **f** Comparison of simulated and experimental lifetimes for hot exciton cooling dynamics with varying excitation energy for **e** 38% Ga and **f** 65% Ga QDs.

well with the lifetimes extracted from the diagonal time trace of the 2DE spectra.

The distinct exciton cooling lifetimes of the two compositions are explained by the intricate interplay between exciton level structure and EXPC strength. In 38% Ga QDs, the presence of a larger energy gap between the $1S_h$ - $1S_e$ and $1P_h$ - $1P_e$ states slows relaxation into the band edge (1.85 eV). Meanwhile, strong diagonal EXPC of states within this gap at ~ 2.02 eV (0.17 eV above the band edge) leads to large reorganization energies, which further stabilizes and retains energy in these states, as shown in Fig. 4.7c, d. In addition, due to the strong off-diagonal EXPC in 38% Ga QDs, energy is initially (before 50 fs) transferred to excitons with higher energy, leading to an initial increase in total energy followed by energy loss. Further, if optical phonons are removed from the calculations, the exciton cooling becomes significantly slower (6 to 10-fold) for both 38% and 65% Ga QDs (Fig. 4.7a, b), indicating the importance of the optical phonons in the cooling process.

Simulated exciton lifetimes for the diagonal signals of the 2D spectra (Fig. 4.7e, f) were determined by preparing the initial excited state at each excitation energy window and monitoring the population decay. The exciton lifetime of all energy windows for 38% Ga QDs is longer than that for 65% Ga QDs, supporting our finding that the phonon-assisted exciton cooling rate is faster for 65% Ga QDs. Our simulations for 65% Ga QDs indicate that excitons with higher energies have shorter lifetimes, which can be attributed to the higher density of excitons and the larger number of relaxation pathways (especially those mediated by optical phonons) for high-energy excitons. The experimental exciton lifetimes for 65% Ga QDs show overall excellent agreement with theory, with a less pronounced decreasing trend. This agreement is attributed to the truncation of upper boundary excitonic states in our simulations, which limits the up-conversion pathway for the 65% Ga system. For 38% Ga QDs, both the experimental and calculated lifetimes follow a nonmonotonic trend with a maximum observed at ~ 2.0 eV. This nonmonotonicity in the 38% Ga system is attributed to “population retaining” excitons between $1S_h$ - $1S_e$ and $1P_h$ - $1P_e$ states (at ~ 2.02 eV) that slow down exciton cooling. The agreement between simulations of pristine alloyed QDs and experiments on femtosecond-timescale exciton dynamics and steady-state characterization (optical and Raman spectra) also demonstrates that our synthesis methods yield high quality samples with minimal defects. The presence of multiple defects would otherwise alter the exciton cooling dynamics and affect the optical and Raman spectra results.

4.4 Conclusions

In conclusion, we have demonstrated the effect of alloying on excited state dynamics and EXPC in emissive $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs with two alloying compositions (38% and 65% Ga) using 2DES and theoretical computations. Incorporation of Ga not only decreases the oscillator strengths of the emissive states, but also introduces complex exciton level structures and dynamics beyond the simple effective mass model. The distribution of direct gap-like and indirect gap-like exciton states follows the same trend as bulk $\text{In}_{1-x}\text{Ga}_x\text{P}$ semiconductors, where 65% Ga QDs show more indirect-like excitons near the band edge with low oscillator

strength as compared to 38% Ga QDs. Higher Ga content also results in lower oscillator strengths of exciton states at higher energy, which leads to unique 2DE spectral lineshapes for 65% Ga QDs. Due to the high density of states and close energy spacings of excitons, optical phonons play a significant role in the femtosecond non-radiative exciton cooling process. In particular, 38% Ga QDs show slower hot exciton cooling due to the presence of “energy-retaining” excitons between the $1S_h$ - $1S_e$ and $1P_h$ - $1P_e$ states, as shown in both experiment and theoretical calculations. We attribute this difference to the fact that the more closely spaced exciton energy levels in 65% Ga QDs facilitate the hot exciton cooling and decoherence processes. Overall, the composition of alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}$ QDs tunes exciton energy spacings and available phonon energies. The interplay between these factors determines EXPC and phonon-assisted relaxation dynamics in this model alloyed QD, suggesting that alloying is an important tool for engineering excited state dynamics and electronic coherences in addition to excited state energies in semiconducting QD systems.

Chapter 5

Summary

In this dissertation, we developed an atomistic, machine-learning-enabled framework for understanding and predicting the electronic structure and excited-state photophysics of semiconductor nanomaterials, with a particular focus on colloidal III-V nanocrystals. By combining methodological development in atomistic pseudopotential theory with direct application to electronic, optical, vibronic, and spectroscopic properties, this work establishes a route toward predictive, computation-driven design in which wavefunction character, exciton structure, and exciton-phonon coupling can be resolved on equal footing.

A central contribution of this dissertation is the development of DeepPseudopot, a machine-learning atomistic semi-empirical pseudopotential framework that reproduces DFT + GW-level electronic structure properties with high fidelity across diverse elemental and compound semiconductors. By combining a neural-network representation of local screened pseudopotentials with physically motivated non-local and spin-orbit coupling terms, DeepPseudopot retains the interpretability of atomistic pseudopotential theory while improving its flexibility, accuracy, and transferability. Trained on a relatively small set of bulk band structures and deformation potentials, it generalizes across crystal phases, bulk alloys, large nanostructures, and alloyed nanostructures without retraining. Extensions to local atomic environment descriptors further suggest a path toward non-periodic systems, including ligands and ligand-semiconductor interfaces.

Building on this foundation, we used atomistic theory to interpret and predict the excited-state photophysics of colloidal III-V nanocrystals. Within the DeepPseudopot framework, key observables including optical gaps, radiative lifetimes, Stokes shifts, excitonic fine structure, and phonon-resolved emission were described in quantitative agreement with experiment on novel colloidal GaAs nanocrystals. This framework was extended to phonon-resolved photoluminescence through an atomistic linear-response description of single-nanocrystal emission. In the case of GaAs nanocrystals, we connected fluorescence line narrowing and photoluminescence excitation measurements to underlying excitonic and vibronic structure, showing that atomistic modeling can directly connect exciton-phonon coupling to experimentally observed spectral line shapes. In alloyed $\text{In}_{1-x}\text{Ga}_x\text{P}/\text{ZnS}$ quantum dots, our method explained the evolution from direct-like to indirect-like optical behavior through changes in

conduction-band-edge character from Γ -like to X -like states. Together, these results show that the photophysics of confined III-V nanocrystals is governed by atomistic wavefunction character and exciton-phonon coupling, extending the simple bulk-like direct-versus-indirect classification.

We further showed that alloying tunes not only static excited-state energies, but also ultrafast exciton relaxation pathways and electronic coherences. In emissive $\text{In}_{1-x}\text{Ga}_x\text{P}$ quantum dots, two-dimensional electronic spectroscopy together with atomistic calculations revealed that increasing Ga content reduces oscillator strength, modifies exciton energy spacings, and reshapes exciton-LO phonon coupling across the excitonic manifold. The comparison between 38% and 65% Ga quantum dots further showed that more closely spaced exciton levels facilitate faster relaxation and decoherence, whereas lower-Ga nanocrystals retain coherence signatures across a broader range of exciton states.

Overall, this dissertation shows that predictive understanding of nanocrystal photophysics requires a unified atomistic description of electronic structure, excitonic structure, and exciton-phonon coupling across multiple length and time scales. Advances in synthesis now provide high-quality colloidal III-V nanocrystals suitable for quantitative comparison with theory, while machine-learning-enhanced atomistic methods make it possible to access the necessary electronic and vibronic resolution beyond the reach of conventional first-principles calculations alone. Looking forward, important directions include more flexible treatments of non-local and spin-orbit terms in DeepPseudopot, incorporation of higher-order exciton-phonon interactions and non-Condon effects, and extension to more thorough modeling of the ligand potentials via the atomic environment descriptor embeddings. More generally, the framework developed here opens a path toward rational, computation-driven design of semiconductor nanocrystals with tailored optical and dynamical properties.

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