



Analysis of Quantum Confinement Effects in Semiconductor Nanostructures for Optoelectronic Applications

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Abstract

Quantum confinement provides a direct route for engineering the electronic and optical behavior of semiconductor nanostructures because carrier motion becomes spatially restricted when one or more dimensions approach the exciton Bohr radius. This methodology paper develops a reproducible theoretical framework for analyzing the size dependence of the effective band gap and the corresponding optical transition wavelength in semiconductor quantum dots, using CdSe as a representative material. The approach combines the effective-mass approximation with the Brus confinement expression, including electron and hole kinetic-energy terms and first-order electron-hole Coulomb attraction. A radius sweep from 2 to 6 nm is used to quantify the transition from strong toward weaker confinement. The computed results predict an optical gap increase from the 1.75 eV bulk value to approximately 2.54 eV at a 2 nm radius, corresponding to a wavelength shift from about 709 nm to 488 nm. The analysis therefore demonstrates the inverse relationship between nanostructure size and transition energy and connects this tunability to light-emitting diodes, lasers, photodetectors, electroabsorption devices and photovoltaic absorbers. The framework is intended as a transparent methodology rather than a replacement for atomistic calculations; surface states, finite barriers, dielectric mismatch and non-parabolic bands are identified as key extensions for device-specific modeling.

Introduction

Semiconductor nanostructures occupy the regime between bulk solids and molecular systems. In a bulk crystal, charge carriers can move over distances much larger than their characteristic quantum-mechanical length scales, producing quasi-continuous electronic bands. When the dimensions of a semiconductor are reduced to the nanometer scale, the allowed carrier wave functions are restricted by physical boundaries and potential barriers. This restriction raises the carrier kinetic energy, converts portions of the band spectrum into discrete states, and shifts the lowest optical transition to higher energy. The foundational effective-mass treatment of small semiconductor

crystallites showed that the lowest excited-state energy should vary strongly with particle size [1], while later calculations established distinct regimes of exciton, intermediate and individual-particle confinement according to the ratio of dot radius to exciton Bohr radius [3].

Quantum confinement is not limited to zero-dimensional quantum dots. Quantum wells confine carriers in one spatial direction, quantum wires confine them in two directions, and quantum dots confine them in all three. These architectures create different densities of electronic states and therefore different absorption, emission and carrier-transport characteristics. A particularly important device

consequence was demonstrated by the quantum-confined Stark effect in GaAs/AlGaAs quantum wells, where an applied electric field produces a large, controllable shift of the absorption edge while excitonic resonances remain pronounced [2]. Thus, confinement is both a materials phenomenon and a device-design variable.

For optoelectronic engineering, size-dependent band-gap control is valuable because it allows spectral response to be tuned without changing the nominal chemical composition. Colloidal quantum dots can be synthesized with nanometer-scale size control and incorporated into solution-processed films, while epitaxial quantum wells and dots can be integrated into semiconductor heterostructures. Reviews of semiconductor nanocrystals have emphasized that confinement modifies absorption thresholds, exciton fine structure, oscillator strengths and carrier interactions [4,6]. Core-shell structures additionally passivate surface states and improve luminescence efficiency, as demonstrated for CdSe/ZnS quantum dots spanning much of the visible spectrum [5].

The purpose of this paper is to present a compact methodology for quantifying confinement-induced optical shifts and interpreting their relevance to optoelectronic applications. CdSe is used as the reference semiconductor because its nanocrystals are extensively characterized and because classical effective-mass parameters are well established. The study is theoretical: it calculates the optical gap as a function of radius, converts that gap into an approximate photon wavelength, and interprets the results against established experimental and device literature. No experimental measurements are claimed. The literature set is restricted to publications from 2019 or earlier, as required for the present review boundary.

Literature Review

Early quantum-size models supplied the conceptual basis for modern nanocrystal optoelectronics. Brus derived an approximate size-dependent expression in which the electron and hole confinement energies increase approximately as $1/R^2$ and are partially offset by an attractive electron-hole Coulomb term that scales approximately as $1/R$ [1]. Kayanuma subsequently showed that the optical response changes across confinement regimes and that oscillator strength can vary substantially when the particle radius becomes comparable to the effective exciton Bohr radius [3]. These results explain why nanoscale dimensions alter not only

the transition energy but also the strength and character of the optical transition.

The broader physical-chemistry perspective developed by Alivisatos highlighted the ability to alter electronic, structural and optical properties through nanocrystal size control [4]. The development of high-quality core-shell quantum dots then addressed a major practical limitation: surface-related non-radiative recombination. Dabbousi et al. reported CdSe/ZnS nanocrystals with size-dependent visible photoluminescence and high room-temperature quantum yields, showing that confinement and surface passivation can be combined to obtain bright emitters [5]. Efros and Rosen later reviewed semiconductor-nanocrystal electronic structure within multiband effective-mass approaches and emphasized the roles of Coulomb interaction, band coupling and exciton fine structure [6].

Quantum confinement also enabled optical amplification. Klimov et al. observed optical gain and stimulated emission in nanocrystal quantum dots at wavelengths tunable by particle size, establishing a route toward quantum-dot lasers [7]. In parallel, quantitative optical characterization improved. Yu et al. demonstrated that the extinction coefficient of CdTe, CdSe and CdS nanocrystals changes strongly with particle size, which is important when converting measured absorbance into nanocrystal concentration and when comparing optical cross sections [8]. These studies collectively connect the electronic structure of confined carriers to measurable device-relevant optical quantities.

As computational treatments became more detailed, the limitations of a simple perturbative confinement model were examined. Şahin et al. used self-consistent Poisson-Schrödinger calculations within the effective-mass approximation to treat a single exciton in spherical CdSe and CdSe/ZnS quantum dots, explicitly showing that electron-hole attraction lowers the excitonic transition energy and modifies carrier localization [9]. Their material parameters provide a convenient reference for the present reproducible calculation. Such self-consistent methods are more physically complete than the closed-form Brus equation, but the latter remains valuable for rapid parameter sweeps, sensitivity analysis and initial device design.

The application literature shows why this tunability matters. Colloidal quantum-dot solar cells exploit solution-processed nanocrystals and adjustable absorption spectra for photovoltaic harvesting [10]. Quantum-dot light-emitting

technologies use the narrow, tunable emission and high luminescence efficiency of colloidal dots to target display and solid-state-lighting applications [11]. Materials-focused reviews have further linked nanocrystal synthesis, surface chemistry, heterostructuring and charge-transport engineering to performance in photovoltaics, photodetectors, lighting, sensing and related optoelectronic systems [12]. A

complementary review of colloidal quantum dots emphasized device architectures and the role of surface treatments and transport layers in LEDs, photodetectors and solar cells [13]. By 2019, the quantum-dot concept had expanded to two-dimensional-derived dots and related low-dimensional structures, with photodetection and broader energy/optoelectronic applications highlighted as active directions [14].

Table 1. Literature-supported physical basis and device relevance of quantum confinement.

Theme	Representative evidence	Method/structure	Relevance to this study
Size-dependent gap	Brus [1]; Kayanuma [3]	EMA / exciton confinement	Basis of radius-dependent energy calculation
Bright emission	Dabbousi et al. [5]	CdSe/ZnS core-shell QDs	Connects confinement to LED/lighting output
Optical gain	Klimov et al. [7]	Nanocrystal QD films	Connects tunable states to laser action
Device translation	Sargent [10]; Shirasaki et al. [11]	Solar cells and QD-LEDs	Links spectral engineering to applications
Modern extensions	Kershaw et al. [12]; Manikandan et al. [14]	Heterostructures and 2D QDs	Shows broader pre-2020 nanostructure landscape

Methodology

A deterministic theoretical workflow was used so that every result can be reproduced from stated material parameters. The model represents a spherical CdSe quantum dot embedded in a sufficiently high barrier such that the lowest electron and hole states can first be approximated by an infinite spherical confinement potential. The calculation then applies the effective-mass approximation and a first-order Coulomb correction, consistent with the physical structure of the Brus model [1] and the confinement-regime analysis of Kayanuma [3]. The resulting optical gap is interpreted as the lowest electron-hole transition. More advanced finite-barrier and self-consistent approaches, such as the method of Şahin et al. [9], are reserved for validation or extension.

Step 1 – Define the reference material. CdSe was selected because it has a bulk gap in the visible/near-infrared boundary region and extensive quantum-dot literature. The numerical inputs were $E_{g,bulk} = 1.75$ eV, electron effective mass $m_e^* = 0.13m_0$, hole effective mass $m_h^* = 0.45m_0$, and relative dielectric constant $\epsilon_r = 9.3$. These values are consistent with the CdSe parameter set used by Şahin et al. [9]. The effective exciton Bohr radius reported in that calculation is approximately 4.88 nm, providing a useful scale for classifying the 2–6 nm radius sweep.

Step 2 – Set the size domain. Spherical dot radii $R = 2.0, 2.5, 3.0, 4.0, 5.0$ and 6.0 nm were evaluated. Radii below the exciton Bohr radius emphasize strong or intermediate confinement, whereas the 5–6 nm points illustrate the approach toward bulk-like behavior. This range also spans particle sizes commonly encountered in CdSe nanocrystal studies [5,8].

Step 3 – Calculate kinetic confinement. For an electron and a hole confined in a spherical region, the lowest-state kinetic contribution was calculated as $\Delta E_{conf} = (\hbar^2\pi^2/2R^2)(1/m_e^* + 1/m_h^*)$. The $1/R^2$ dependence is the dominant reason the effective gap increases rapidly when R becomes small [1].

Step 4 – Apply electron-hole attraction. The first-order Coulomb correction was calculated as $E_{coul} = 1.8e^2/(4\pi\epsilon_0\epsilon_r R)$. Because the electron and hole attract, this term is subtracted from the kinetic increase. The correction grows as size decreases but only as $1/R$, so the positive $1/R^2$ confinement term dominates in sufficiently small dots [1,3].

Step 5 – Obtain the effective optical gap. The modeled lowest optical transition was evaluated using $E_g(R) = E_{g,bulk} + \Delta E_{conf} - E_{coul}$. This form captures the leading quantum-size trend while retaining transparent physical meaning. It does not explicitly include surface polarization, finite barrier leakage, non-parabolicity, crystal-field splitting or detailed exciton fine structure [6,9].

Step 6 – Convert energy to wavelength. For optoelectronic interpretation, the approximate transition wavelength was calculated from $\lambda(\text{nm}) = 1240/E_g(\text{eV})$. A higher confined transition energy therefore corresponds to a shorter wavelength (blue shift).

Step 7 – Interpret device relevance. Calculated gap and wavelength shifts were compared with the spectral-control requirements of LEDs, lasers, photodetectors, electroabsorption devices and photovoltaic absorbers discussed in prior literature [2,7,10–13]. The model is used to identify trends rather than to predict a complete device efficiency.

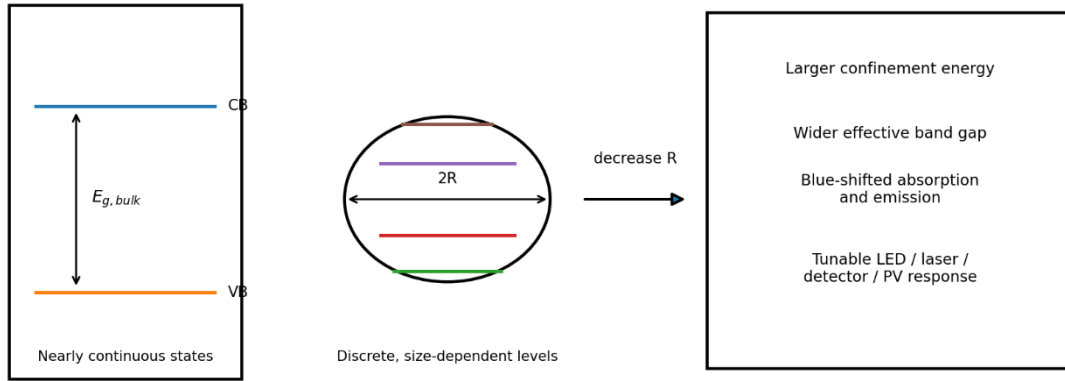


Figure 1. Conceptual link between nanoscale carrier confinement, discrete states and tunable optoelectronic response (author-generated schematic).

Results

The calculation produces a monotonic increase in the effective CdSe optical gap as the quantum-dot radius decreases. At $R = 6$ nm, the predicted gap is about 1.81 eV, only 0.06 eV above the bulk value, indicating relatively weak size influence. At $R = 4$ nm, the predicted gap rises to approximately 1.91 eV. When the radius is

reduced to 3 nm, the gap reaches about 2.07 eV, and at $R = 2$ nm it reaches approximately 2.54 eV. The corresponding optical wavelength moves from about 686 nm at 6 nm radius to about 488 nm at 2 nm radius. This strong blue shift is the central signature of quantum confinement and is consistent with the qualitative behavior established in foundational and experimental nanocrystal studies [1,5,8].

Table 2. Calculated quantum-confinement response of spherical CdSe quantum dots.

Radius R (nm)	Diameter (nm)	ΔE_{conf} (eV)	E_{coul} (eV)	$E_g(R)$ (eV)	λ (nm)
2.0	4.0	0.932	0.139	2.543	488
2.5	5.0	0.597	0.111	2.235	555
3.0	6.0	0.414	0.093	2.071	599
4.0	8.0	0.233	0.070	1.913	648
5.0	10.0	0.149	0.056	1.843	673
6.0	12.0	0.104	0.046	1.807	686

The numerical decomposition also shows why the trend is strongly nonlinear. At 2 nm radius, the kinetic confinement term is approximately 0.93 eV, whereas the Coulomb attraction is approximately 0.14 eV. At 6 nm radius, these terms fall to about 0.10 eV and 0.05 eV, respectively. Hence, shrinking the nanostructure produces a much faster increase in kinetic quantization than in Coulomb stabilization. The resulting curve steepens strongly below roughly 3–4 nm, which is precisely the regime where the nanostructure size is below the CdSe exciton Bohr radius and the strong-confinement approximation becomes most relevant [3,9].

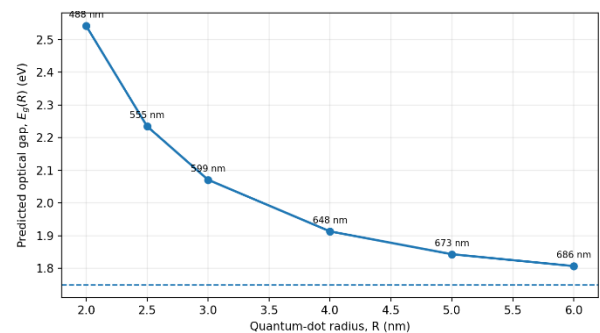


Figure 2. Predicted CdSe optical gap versus quantum-dot radius; labels show the

corresponding photon wavelength (author-generated calculation).

Conclusion and Discussion

The results demonstrate that quantum confinement can serve as a practical spectral-engineering mechanism in semiconductor nanostructures. For the CdSe case studied here, reducing radius from 6 to 2 nm changes the predicted lowest optical transition from approximately 1.81 to 2.54 eV, corresponding to a shift from red-region emission/absorption toward the blue-green region. The magnitude and direction of this change follow directly from the competition between positive kinetic confinement and negative electron-hole Coulomb attraction. Because the kinetic term scales as $1/R^2$, it becomes dominant at small radii and produces the characteristic blue shift. This trend explains several established optoelectronic opportunities. In quantum-dot LEDs, controlled size distributions allow the emission color to be selected through confinement while shell growth and surface passivation suppress non-radiative losses [5,11]. For nanocrystal lasers, confinement supplies tunable gain wavelengths, although Auger recombination and multiexciton dynamics must be managed [7]. In photodetectors and photovoltaic absorbers, changing the gap can shift the onset of absorption and improve spectral matching; however, charge extraction, surface traps, ligand barriers and energetic alignment with transport layers remain as important as the nanocrystal gap itself [10,12,13]. Quantum wells provide a related but structurally distinct mechanism in which confinement and electric field can be combined to modulate absorption through the quantum-confined Stark effect [2]. The simple model is intentionally transparent and therefore has limitations. First, it assumes a spherical dot and an infinite confining barrier, while real core-shell or matrix-embedded nanocrystals have finite band offsets and wave-function leakage. Second, effective masses and dielectric constants are treated as bulk-like and independent of size. Third, the model neglects surface polarization, ligand-induced states, dielectric mismatch, non-parabolic bands, crystal-field effects and atomistic symmetry. Fourth, it converts the calculated excitonic gap directly to a wavelength and therefore does not separately model Stokes shift, phonon coupling or defect-mediated emission. Self-consistent Poisson-Schrödinger methods [9] and multiband/atomistic approaches [6] should be used when quantitative agreement with a specific nanostructure or device is required. Within these boundaries, the methodology is useful because it is reproducible,

computationally light and physically interpretable. It can be extended by replacing CdSe parameters with those of another semiconductor, introducing finite barrier heights, adding a size distribution, or coupling the calculated optical gap to transfer-matrix and drift-diffusion device models. The literature available up to 2019 shows a consistent progression from fundamental confinement theory [1,3] to bright core-shell emitters [5], optical gain [7], solution-processed photovoltaics [10], quantum-dot LEDs [11], and increasingly diverse low-dimensional quantum-dot families [14]. The analysis therefore supports the conclusion that nanostructure size is a first-order design variable for tailoring semiconductor optoelectronic response, but device performance ultimately depends on the combined optimization of confinement, interfaces, surfaces and charge transport.

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