As an intrinsic feature of any quantum system, coherence has attracted considerable attention due to its possible role in energy and charge transfer in nanoscale and biological systems.\textsuperscript{1−15} The development of ultrafast multidimensional coherent spectroscopies has led to the discovery of time-dependent oscillatory signals in biological and man-made light harvesting systems at room temperature.\textsuperscript{6,16,17} These oscillations are interpreted as quantum beating due to a coherent superposition of electronic states with a well-defined relative phase.\textsuperscript{1} The oscillation frequency is dictated by the energy gap between the participating electronic states. The longer this oscillation remains intact, the longer is the quantum coherence.\textsuperscript{18,19} The knowledge of the decoherence time is of fundamental importance to light harvesting, optoelectronic, spintronic, lasing, quantum computing, and other applications of semiconductor nanocrystals. It sets the time scale for which the operations based on coherent light−matter interactions can occur in a given material. Typically, long coherence times are desired.\textsuperscript{2,6,11,20}

Many factors contribute to the loss of quantum mechanical phase. In bulk materials with continuous electronic spectra, the dephasing is mainly associated with quantum transitions due to carrier−carrier and carrier−phonon scattering, carrier recombination, Auger-type phenomena, etc.\textsuperscript{21,22} In comparison, transitions are slow in quantum systems with discrete electronic spectra, and dephasing happens elastically, without change in population of the participating states. Called pure dephasing,\textsuperscript{23,24} this process sets a firm time limit for which a coherent system can progress through the Rabi cycle.\textsuperscript{25,26} Decoherence is a consequence of the fact that a quantum system can never be completely isolated. Its interactions with the surrounding environment will eventually destroy phase correlations, leading to decoherence.

Both ensemble effects (inhomogeneous broadening) and coupling to the bath (homogeneous broadening) result in fast dephasing, thus contaminating and challenging the detection of electronic coherence.\textsuperscript{27} Several reported electronic coherence studies remain controversial highlighting the challenges in experimental detection. To rationalize the long-lived coherences that last for hundreds of femtoseconds, several models invoking strong correlation in the mechanism of decoherence have been proposed. It has been shown that resonant lattice
vibrations (phonons) play an essential role. Coupling with the same phonon modes results in a correlated evolution of the excitons, enabling long-lived coherences. However, electron-nuclear correlation is not the only factor that can lead to the development of long-lived coherences. A small magnitude of the fluctuation in the energy gap between the electronic states is generally needed to sustain coherence, and a small energy gap can also lead to a small fluctuation. Independent bosons lead to the simplest model of excitonic coherence and the key sources of coherence loss, established for the well-defined core/shell NPLs, should apply to other nanoscale systems.

Constrained by the large number of atoms in the present problem, and aiming to perform time-domain atomistic simulation with a reasonable computational cost, we carried out all quantum-mechanical calculations, including geometry optimization, electronic structure, and adiabatic molecular dynamics (MD), with the self-consistent charge density functional tight binding (SCC-DFTB) method as implemented in the DFTB+ code. The parameter set (Slater-Koster files) used in this calculation were extensively tested for a variety of Cd-chalcogenide systems. Among the different morphologies, two-dimensional nanoplatelets (NPLs) draw particular attention because of their large absorption cross-section and narrow spectral line widths. The NPL structural pattern leads to strong anisotropic quantum confinement. Owing to their considerably larger intraband absorbance, as compared to quantum dots, NPLs are more desirable for light-harvesting applications. The absence of ensemble disorder and narrow spectral line shapes makes colloidal NPLs an ideal system to study electronic coherence and gain insight into its role in charge and energy transfer. A significant body of work has been reported on these high-quality nanosystems, focusing on coherent quantum dynamics of excitons. The recent observation of quantum beats in colloidal CdSe and CdSe/CdZnS core/shell NPLs at room temperature was attributed to a coherent superposition of the heavy hole (HX) and light hole (LX) excitons. The beats were characterized using 2D electronic spectroscopy by Scholes and co-workers. By synthesizing NPLs with precisely controlled thickness, the authors minimized the inhomogeneous broadening and observed dephasing times in the range of 13–24 fs for both CdSe and CdSe/CdZnS core/shell NPLs. The exact knowledge of the system size creates an excellent opportunity for an atomistic simulation, which can reproduce directly the experimental setup. In addition, atomistic modeling takes into consideration interfacial interactions, core/shell interpenetration, defects, and other realistic details that are inevitably present in experiment.

In this Letter, we elucidate the atomistic origin of the long-lived coherence between heavy and light hole excitations in CdSe and CdSe/CdZnS core/shell NPLs, including both pristine systems, and NPLs with cationic and anionic defects caused by cross diffusion at the core/shell interface. Based on density functional theory (DFT), our molecular dynamics simulations directly mimic the experiment of Scholes and co-workers, showing excellent agreement with the measured coherence times. The simulations demonstrate that long coherence arises due to small fluctuations in the energy gap between the heavy and light hole excitations, as well as due to a relatively slow decay of the correlation between the heavy and light hole energies. The gap fluctuation is an order of magnitude smaller than thermal energy. Since both heavy and light holes couple to the same phonon modes, their energy fluctuations can synchronize, minimizing coherence loss. The electronic structure calculations demonstrate that the excitations are localized near NPL surfaces. Hence, coupling to surface acoustic phonons constitutes the main source of decoherence, and atom exchange at a core/shell interface provides additional decoherence channels. Surprisingly, the exchange of Se and S atoms that form the core and shell valence bands has little effect on the coherence time. On the contrary, the exchange of Cd and Zn that contribute to the conduction bands has a major effect on the electronic coherence properties in the relevant energy range. The atomistic understanding of the origins of the long-lived coherence and the key sources of coherence loss, established for the well-defined core/shell NPLs, should apply to other nanoscale systems.

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NPLs was exactly the same. Two (2) unit layers of the CdZnS shell were added on each side of the core, resulting in a total of 9 unit layers, and 288 Cd, Se, Zn, and S atoms in the simulation cell. Figure 1b represents the optimized CdSe/CdZnS core/shell NPLs, whereas Figures 1c and d represent the optimized structures corresponding to the core/shell NPLs with anionic defects (Se/S atoms exchanged) and cationic defects (Cd/Zn atoms exchanged) at the interface, respectively. The arrows indicate each Se/S or Cd/Zn atom pair exchanged at the interface between core and shell. In all cases, we chose the stoichiometric 1010 nonpolar surface derived from the wurtzite bulk, and the NPLs were constructed in accordance with the experimental work by Scholes and co-workers. 

The coherence times between pairs of optical excitations in the NPLs are characterized by computing and analyzing the pure-dephasing times calculated using the optical response theory.30 The phonon-induced fluctuations in the energy gap between the states are characterized by the autocorrelation function (ACF).

\[
C(t) = \frac{\Delta E(t)\Delta E(0)}{\Delta E^2(0)}
\]

The brackets indicate canonical averaging. The ACF is normalized

\[
C_{\text{norm}}(t) = \frac{\Delta E(t)\Delta E(0)}{\Delta E^2(0)}
\]

by its initial value \(C(0) = \Delta E^2(0)\). The square root of this value gives the average fluctuation of the energy gap. The pure-dephasing function is computed using the second-order cumulant expansion to the optical response function:30

\[
D_{\text{cumu}}(t) = \exp(-g(t))
\]

where \(g(t)\) is given by

\[
g(t) = \int_0^t dr_1 \int_0^{r_1} dr_2 C(\tau_2)
\]

The electronic energy gaps used for the computation of the coherence times were obtained using the Kohn−Sham orbital energies from the ground state DFTB calculations. The optical spectra were also computed in the Kohn−Sham representation to correspond to the energy levels used in the coherence time calculations.

Depending on the core and shell thickness, a CdSe/CdZnS heterostructure shows type-I, type-II, or quasi type-II band alignment.60,61 The partial density of states (PDOS) of the optimized structures of the CdSe, CdSe/CdZnS core/shell NPLs are given in Figures S1a and S1b of Supporting Information, respectively. The PDOS plot for the CdSe NPLs shows that Se atoms contribute to the valence band maximum (VBM), whereas contribution to the conduction band minimum (CBM) mainly comes from Cd atoms. The VBM of the core/shell structure arises from the core, while CBM stems from the shell resulting in an overall type-II band alignment.

The room-temperature optical spectrum of CdSe NPLs is shown in the inset of Figure 2a, in which the dotted red line indicates individual transitions, while the black curve
corresponds to Gaussian broadened peaks. Following the notation of the experimental paper, two different heavy hole excitons (HX), labeled as HX1 and HX2 with the average energy of 2.37 and 2.41 eV, and three different light hole excitons (LX), labeled as LX1, LX2, and LX3 with the average energy of 2.46, 2.48, and 2.56 eV, are identified. Table 1 summarizes different HX and LX transition energies for the CdSe NPLs. To determine the pure-dephasing time between HX and LX, a total of six pairs of excitons, namely, HX1–LX1, HX1–LX2, HX2–LX1, HX2–LX2, and HX2–LX3 have to be considered. The average energy differences between HX and LX excitons range from 0.34 to 0.15 eV, Table 1. We focus on the two pairs, HX1–LX1 and HX2–LX3, that are closest to the experimental data. The energy gaps between these pairs are within 15% from the experimental value of 0.14 eV. The pure-dephasing functions of these two exciton pairs are shown in Figure 2b.

The room-temperature optical spectrum for the CdSe/CdZnS core/shell heterostructure is shown in the inset of Figure 3a. Here, there is only one significant transition in the HX peak, labeled as HX1 with an average energy of 2 eV, and three different LX excitons, labeled as LX1, LX2, and LX3 with the average energies of 2.16, 2.20, and 2.23 eV, respectively. Table 2 summarizes different HX and LX optical transition energies for the CdSe/CdZnS core/shell NPLs and shows the canonically averaged energy difference between various exciton pairs. A total of three pairs of HX–LX excitons, namely, HX1–

<table>
<thead>
<tr>
<th>no.</th>
<th>HX</th>
<th>E (eV)</th>
<th>LX</th>
<th>E (eV)</th>
<th>ΔE_{exp} (LX–HX)</th>
<th>ΔE (eV)</th>
<th>(\delta(\Delta E)^2) (meV^2)</th>
</tr>
</thead>
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<tr>
<td>1</td>
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<td>0.08</td>
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<td>LX3</td>
<td>2.56</td>
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<td>0.15</td>
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<td>LX3</td>
<td>2.56</td>
<td></td>
<td></td>
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<tr>
<td>6</td>
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</table>

“Experimental, \(\Delta E_{exp}\), and calculated, \(\Delta E\), energy gaps between heavy and light hole excitations, and square gap fluctuation \(\delta(\Delta E)^2 \equiv (\Delta E – \overline{\Delta E})^2\).”

summarizes different HX and LX transition energies for the CdSe NPLs. To determine the pure-dephasing time between HX and LX, a total of six pairs of excitons, namely, HX1–LX1, HX1–LX2, HX1–LX3, HX2–LX1, HX2–LX2, and HX2–LX3 have to be considered. The average energy differences between HX and LX excitons range from 0.34 to 0.15 eV, Table 1. We focus on the two pairs, HX1–LX1 and HX2–LX3, that are closest to the experimental data. The energy gaps between these pairs are within 15% from the experimental value of 0.14 eV. The pure-dephasing functions of these two exciton pairs are shown in Figure 2b.

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![Figure 1](image1.png)

**Figure 1.** (a) Room temperature pure-dephasing functions for pairs of heavy and light hole excitations in the CdSe/CdZnS core/shell nanoplatelet. The red and blue lines represent the HX1–LX1 and HX1–LX2 excitation pairs, whose energy differences most closely match the experiment, Table 2. The inset in panel a displays the optical spectrum. The individual transitions shown by the red line are Gaussian-broadened to obtain the black line. (b) Autocorrelation functions of the energy gaps between the same pairs of excitations. (c) Fourier transforms of (i) HX1, (ii) LX1, and (iv) LX2 excitation energies.
LX1, HX1–LX2, and HX1–LX3, are possible, for which the average energy differences are 0.16, 0.20, and 0.23 eV, respectively. The experimental HX–LX average energy difference is found to be 0.18 eV. Hence, we choose the two pairs of excitons, HX1–LX1 and HX1–LX2, as their energy difference is within 15% of the experimental value. The dephasing functions of these pairs of excitons are shown in Figure 3b.

The data of Tables 1 and 2 indicate that the HX and LX excitation energies are lower for the CdSe/CdZnS core/shell NPLs compared to the CdSe NPLs, while the HX-LX splitting is increased. This is in excellent agreement with the experimental results of Scholes and co-workers. The redshift of the spectra for the core/shell system can be explained by the type-II alignment of the core and shell energy levels and the primary contribution of the core to the VBM, and the shell to the CBM, Figure S1.

The room temperature pure-dephasing functions for the selected pairs of excitons in the CdSe and CdSe/CdZnS core/shell NPLs are plotted in Figures S2a and S3a, respectively. The dephasing times are computed by fitting to the Gaussian, \( f(t) = A \exp\left(-0.5\left(t/t_1\right)^2\right) \). The dephasing times 18.51 and 17.27 fs computed for the CdSe NPL are in excellent agreement with the experimentally measured time of 16 ± 3 fs. The dephasing times computed for the CdSe/CdZnS core/shell NPL are 25.5 and 11.57 fs, which is also consistent with the experimental value of 24 ± 3 fs. In addition to calculating the dephasing times for individual pairs of transitions in the HX and LX peaks, we also calculated the dephasing times for averaging the energies all transitions in the HX and LX peaks. The values are 34.31 fs for the CdSe NPL and 30.86 fs for the CdSe/CdZnS core/shell NPL, Figures S2a and S2b, respectively.

According to the second-order cumulant approximation analysis, eqs 3 and 4, the coherence time is determined by the unnormalized ACF, eq 1, for the energy gap between the pairs of states forming a coherence superposition. In turn, the unnormalized ACF can be analyzed in terms of its initial value, \( C(0) = \Delta E^2(0) \), corresponding to the energy gap fluctuation, and the time scale of decay of the normalized ACF, eq 2. Coherence is long-lived if the energy gap fluctuation is small and/or if the decay of the normalized ACF is slow. The energy gap fluctuations for the core and core/shell NPLs are given in the last columns of Tables 1 and 2, while the normalized ACFs are shown in Figures 2b and 3b. Both factors contribute to the coherences observed in the systems under investigation. The energy gap fluctuations are small, on the order of 1 meV. This is much smaller than thermal energy at room temperature, 25 meV. The ACFs decay on the same time scale as the pure-dephasing functions and exhibit a series of recurrences. The faster decay of the pure-dephasing function for the HX1–LX2 exciton pair, compared to the HX1–LX1 pair in the CdSe/CdZnS NPLs, Figure 3, is due to the larger gap fluctuation, Table 3, rather than faster ACF decay. In general, the ACFs decay faster in the core/shell heterostructure than in the core NPL, because a broader range of phonon modes is available in the system composed of more types of atoms.

In order to identify the phonon modes that couple to the electronic subsystems and induce coherence loss, we computed Fourier transforms (FT) of the excitation energies of the states forming coherent superpositions, Figures 2c and 3c. These influence (power) spectra show more frequencies for the CdSe/CdZnS NPL than for CdSe. This should be expected, because the core/shell system has a broader range of vibrations, and since the VBM and the CBM reside on core and shell, respectively, such that the excitations involve both subsystems. Particularly important for the long-lived coherence, the influence spectra for the HX and LX excitations reveal very similar frequencies. It is true for both CdSe and CdSe/CdZnS NPLs. By coupling to the same phonon modes, the HX and LX excitations exhibit similar fluctuations that maintain correlations for a fairly long time.

The phonon peak appearing below 100 cm\(^{-1}\) can be attributed to the discrete longitudinal acoustic mode as well as the surface acoustic mode, whereas the mode around 200 cm\(^{-1}\) is due to the longitudinal optical phonon of CdSe. The surface optical phonon modes together with the LO modes that have a signature in the range of 350–400 cm\(^{-1}\) also couple with these excitons. These phonon modes are associated with the surface atoms of the NPLs, indicating that the electronic states have contributions from the surface. The frequencies appearing around 400 cm\(^{-1}\) correspond to the first overtone of the LO modes.

Figure S3 presents charge density distribution of the key orbitals of the CdSe and CdSe/CdZnS NPLs contributing to the HX and LX excitations. The charge densities are mainly localized on the NPL surfaces and extended toward the core in a few cases. The orbital localization rationalizes why the major contribution to the loss of quantum coherence in the electronic subsystems arises from the surface phonon modes with a few bulk modes contributing as well.

Given the successful interpretation of the decoherence mechanism of the CdSe and CdSe/CdZnS NPLs, we extended our calculations to structures containing interfacial defects. The primary goal was to understand whether defects, that are inevitably present in experimental systems, have a strong influence on the electronic coherence. Cross diffusion of atoms across interface is common in core/shell materials. We consider two complementary situations, cationic exchange and anionic exchange. The former involves exchange of Cd and Zn atoms, whereas the latter is the exchange of S and Se atoms. The optimized structures for the core/shell systems with the anionic and cationic exchange are shown in Figure 1c and d, respectively. The calculation of the room-temperature spectrum of the cationic defect structure, Figure S2b, reveals that such defects have a strong influence on the optical properties. The obtained spectrum no longer shows well-resolved peaks in the energy range of interest. The cationic atoms (Cd, Zn) are larger than the anionic atoms (Se, S). As a result, the geometric structure is more sensitive to defects in the larger cationic sublattice, and a stronger perturbation in the geometric structure induced by the cationic exchange leads to a stronger

<table>
<thead>
<tr>
<th>no.</th>
<th>HX</th>
<th>E (eV)</th>
<th>LX</th>
<th>F (eV)</th>
<th>( \Delta E ) (eV)</th>
<th>( \delta(\Delta E)^2 ) (meV(^2))</th>
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</table>
perturbation in the optical properties. Thus, the cationic defects are not desirable for sustained excitonic coherence in the CdSe/CdZnS NPLs for the considered excitation energy range. The scenario is completely different for the anionic defect structure. Both excitonic bands are retained and remain well-resolved, as in Figure 4a inset. Table 3 lists different HX and LX transitions that are involved in this particular case, along with the corresponding canonically averaged energies, energy differences, and their fluctuations. There are three different HX excitons HX1, HX2, and HX3 with the average energies of 1.98, 2.03, and 2.10 eV, respectively, and two different LX excitons, LX1 and LX2 and the energies of 2.14 and 2.26 eV. The pure-dephasing functions shown in Figure 4a demonstrate coherence times within the 11−21 fs range, which only slightly faster than the 14−25 fs coherence times for the pristine core/shell system, Figure 3a. Hence, the anionic defect has only a minor influence on the electronic coherence within the electronic subsystem.

The small influence of the anion exchange at the CdSe/CdZnS interface on the coherence time is supported by comparison of the energy gap fluctuations, ACF decay, phonon influence spectra and orbital localization to those of the pristine system. The gap fluctuations are still within 1−5 meV, Table 3, much less than the thermal energy of 25 meV. The ACFs computed for all excitation pairs in the defected heterostructure, Figure 4b, decay similarly to those for the pristine core/shell system, Figure 3b. FTs of the fluctuations of the HX1, HX2, HX3, LX2, and LX3 electronic transitions, Figure 4c, exhibit frequencies that match those of Figure 3c. The low-frequency phonons below 100 cm−1 correspond to surface acoustic modes, while the phonons peaks around 150−200 cm−1 are due to surface optical modes. The introduction of defects disrupts the longer-range acoustic motions, decreasing the low-frequency spectral response. At the same time, defect modes and optical modes have similar frequencies, and therefore, the spectral signal in the optical mode range is enhanced. The stronger coupling of the higher frequency phonons to the HX and LX transitions in the CdSe/CdZnS NPL with the S/Se atom exchange explain why decoherence proceeds 10−15% faster compared to the pristine system. Since the loss of coherence between the HX and LX transitions is induced primarily by surface phonons, modifications of the bulk core region of the nanoplatelets should not significantly reduce the coherence time. Our calculations suggest that it is particularly important to control defects at nanoplatelet surfaces and core/shell interfaces.

To summarize, we have established the atomistic origin of room-temperature coherence between the light-hole and heavy-hole excitations in two-dimensional CdSe and CdSe/CdZnS core/shell nanoplatelets, synthesized and studied recently by
The fundamental principles underlying coherence on nanosystem surfaces, rationalizing coupling to the surface phonons. The computed 18 fs coherence time in the CdSe platelet is in excellent agreement the experimental 16 ± 3 fs value. The 14–25 fs coherence times computed for the core/shell system agrees well with the measured 24 ± 3 fs time. The relatively long coherence is maintained due to small energy gap fluctuations, which are an order of magnitude less than thermal energy, and because of a slow decay of correlation between the heavy and light hole energies. Two different scenarios emerge when defects are introduced at the core/shell interface. Anionic defects prove harmless, and a coherence lifetime of the same order of magnitude is obtained. However, the system with cationic defects does not show well-resolved peaks in the energy range of interest, indicating that it would be hard to obtain sustained coherence in this case. Coherence is maintained due to correlated evolution of the heavy-hole and light-hole excitons that couple to the same phonon modes, including surface acoustic modes below 100 cm⁻¹, surface optical at around 180 cm⁻¹, and to a smaller extent, higher frequency modes in the 350–400 cm⁻¹ range. The charge densities of the key electronic orbitals reveal their localization on nanosystem surfaces, rationalizing coupling to the surface phonons. The fundamental principles underlying coherence loss in the CdSe and CdSe/CdZnS nanoplatelets can be used to design other nanoscale systems with long-lived quantum coherence.

**REFERENCES**