hole relaxation was then attributed by the authors to the opening of a gap in the excitonic manifold between an "absorbing" state $E^{U}_{\pm 1}$ and an "emitting" state $E^{L}_{\pm 1}$.[8] Analysis[9] shows that $E^{U}_{\pm 1}$ is a $\{h_2, e_1\}$ (i.e., electron ground state and second hole state) derived exciton, whereas $E^{L}_{\pm 1}$

different dots (it is located between levels h_{12} and h_{13}, i.e., at $E_v - 180$ meV, in $Cd_{534}Se_{527}$; between h_{13} and h_{14}, i.e., at $E_v - 270$ meV, in $Cd_{232}Se_{235}$; and between levels h_{15} and h_{16}, i.e., at $E_v - 420$ meV, in $Cd_{83}Se_{81}$).[15] Both gaps can effectively slow the hole relaxation process. It is important to notice that the gaps originate from h_4 and h_5 and deeper states and not from h_1 and h_2, as implied by Xu and coworkers.[7]

Possible explanations of the origin of the gaps within the valence band could be: (i) the wurtzite structure and the resulting crystal field splitting; (ii) some special features specific to the CdSe material; (iii) an effect of the dot passivation, or, finally, (iv) the shape of the NC. To investigate these aspects further, we performed additional calculations for a spherical InAs zinc blende, colloidal dot ($In_{456}As_{615}$), with the same dimensions ($R = 19$ Å) as the $Cd_{534}Se_{527}$ dot. For this dot the single-particle problem was solved by expanding the dot wave functions as a linear combination of bulk Bloch states (LCBB).[16] The dot was passivated by emb19dot was

between the states

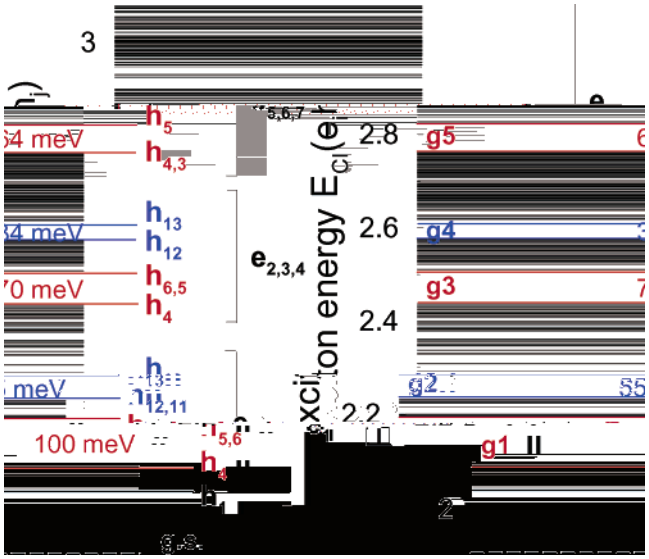

Figure 6. CI excitonic spectrum for $Cd_{534}Se_{527}$. We denote the single-particle origin of the excitons in terms of the levels with high contributions to the CI states.

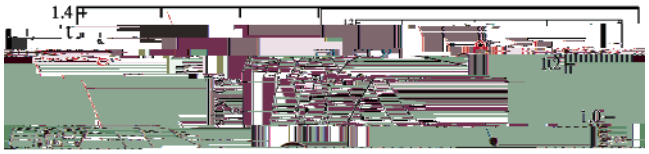

Figure 8. Changes in slope of the hole energy-loss curve (i.e., the time delay t_d of the "hot" PL maximum with respect to a pump pulse [see inset], plotted as a function of the detection energy): experimental data for a 1.8 nm dot (solid circles, solid line, and HELR values) and theoretical predictions for a 1.9 nm dot (the red and blue arrows mark the upper energy end of the gaps). The dotted, dashed and dash−dotted lines emphasize the different slopes in the experimental energy-loss curve (HELR = dE/dt_d). The green arrows indicate the positions of the first experimental points that determine a new slope in the curve. The black arrow indicates the position of the measured 1S absorption, around which position Xu and co-workers[7] identify the only change in slope in the HELR they consider.

Figure 7. CdSe: excitonic energy gaps calculated in the single-particle (SP, empty circles and solid lines) and CI (solid squares and dashed lines) approach, plotted as a function of NC radius.

with decreasing dot size; (ii) conversely, E_{g2} is rather independent of R; (iii) both E_{g1} and E_{g2} are almost unaffected by many-body effects (the single-particle results almost coincide with the CI ones, excepted for the $R = 14$ Å dot); (iv) many-body effects reduce higher gaps (the ones derived from excited electron states) compared to their single-particle values, with larger effects the smaller the dot (see curve relative to g3 in Figure 7). Therefore the *existence* of the gaps is a single-particle effect whereas their *width* is influenced by many-body effects.

Finally we compare our predictions with experiment. Figure 8 shows the measured energy-loss curve[7] for a 1.8 nm CdSe NC (solid circles and lines). Xu and co-workers[7] have identified two slopes in that curve, with the change of slope occurring close to the energy of about 2.22 eV, corresponding to the measured position of the 1S absorption resonance, indicated by a vertical black arrow. This implies the existence of a single gap within the valence band, located around $\sim E_v - 70$ meV for that specific dot size. Analysis of their data, however, reveals three different slopes in the energy-loss curve, indicated by the extrapolated lines in Figure 8. These slopes correspond to the initial HELR (dotted line), the HELR after g2 (dashed line), and the HELR after g1 (dash−dotted line). Since the experimental configuration consists of a hot hole h_n and a ground-state electron e_1, no gap other than g1 and g2 is relevant in Figure 8 (higher gaps involve different electron states). We see that our identification of two gaps (Figures 3 and 6) is consistent with the appearance of three slopes in the measured energy-loss curve. Furthermore, the calculated positions of the change in slope (2.29 and 2.19 eV, indicated by blue and red arrows in Figure 8) are in good agreement with the experimental curve,[21] considering that the calculations were performed for a slightly larger dot than the experimental one, which yields energy values shifted slightly to the red, compared to those relative to the experimental dot. The presence of a gap (g2) between two sets of closely spaced energy levels, could, however, also generate a step-like jump in the delay time, where the hole relaxation would be fast above the gap, slow across the gap, and then fast again below the gap, with the slope being approximately the same above and below the step. The parallel dotted lines in Figure 8 show that this scenario is also supported by the experimental data: due to the large energy interval between two consecutive experimental points, such jump in the delay time could have occurred anywhere between the two measurements at 2.38 and 2.65 eV and have been therefore undetected. The (dotted) line through the points at 2.27 and 2.38 eV is consistent with a parallel to

the (dotted) line passing through the experimental points for higher energies. It has to be mentioned, however, that the first change of slope (the first reduction of the HELR) might also be within the experimental error, whereas the second is definitely not. In other words, the slopes of the dotted and dashed lines in Figure 8 might be the same within experimental error, whereas the dash−dotted line has an indisputably different slope. That is probably the reason Xu et al. in their work[7] only referred to the latter change of slope (black arrow). It has to be pointed out, however, that whereas Xu and co-workers[7] situate the drop in the HELR at energies just *below* the first absorption peak 1S (located at 2.2 eV, black arrow in Figure 8), according to our calculations (see Figure 6), both gaps are found at energies *above* the 1S absorption (which is due to exciton levels originating from h_1, h_2 and e_1). Judging from the experimental curve alone, though, it cannot be excluded that the decrease in the HELR occur just above 2.2 eV, the last experimental point before the change of slope being at 2.27 eV and the next at 2.16 eV.

Based on the similarities found between the hole manifolds in CdSe and InAs NCs, and the fact that the LO phonon energies in both bulk materials are also very similar ($\hbar\omega_{\mathrm{LO}}^{\mathrm{CdSe}}$