# The Peculiar Electronic Structure of PbSe Quantum Dots

and therefore exaggerating the degree of quantum confinement (d). Tight-binding calculations[14,15] incorporate in principle all four effects (a−d). However, the tight-binding fit[14] to the bulk band structure of PbSe had missed most of the L-valley anisotropy: $m_l/m_t = 0.0374/0.0462 = 0.81$ was used for electrons instead of the experimental 0.070/0.040 = 1.75 (see ref 19) and 0.0468/0.0472 = 0.99 was used for holes instead of the experimental 0.068/0.034 = 2.0. Consequently, effect (c) was improperly accounted for. We conclude that the splittings of L states in PbSe dots have not been properly understood or predicted, and thus the near-edge absorption spectra of the dots remain unexplained. We will show that a proper inclusion of effects (a)−(d) correctly reproduces both the intraband and the interband absorptions of PbSe dots.

(ii) *What is the origin of the observed interband absorption peaks?* Experimentally, it is possible to resolve three peaks in the absorption spectrum of ensembles of PbSe nanocrystals.[3,4,6,8,11,15,16] On the basis of the coincidence between the measured and k•p calculated transition energies, it was suggested[11] that the three observed assisted electron cooling should be slow, and thus other scattering mechanisms are required to explain the observed picosecond electron cooling rate. As shall be shown below, an atomistic calculation of the energy levels of PbSe dots indicates that hole states are much more dense than electron states (viz. Figure 1) because hole states arise not only from L points but also from Σ points (viz. Figure 2). The atomistic calculation thus invalidates previous expectations of electron−hole mirror symmetry and the presumed far-reaching consequences[10,16,21] of such an effect.

Our work is aimed at understanding the three puzzles (i−iii) noted above.

**Method of Calculation.**

The transition energies of $\alpha$ and $\beta$ can also be estimated by the DOS peak separations corresponding to the transition assignments in Table 2: $\alpha \approx 1_e - 2_e = 0.144$ eV (measured: 0.145 eV); $\beta \approx 1_e - 3_e = 0.278$ eV (measured: 0.272 eV); $2_e - 3_e$ eV with having different final states ($S_e$ for the first and $P_e$ for the second, respectively). This is related to the fact that the experiment of ref 4 pertains to a highly charged dot, not to a neutral dot. Such high charging will repel the electron and attract the hole resulting from an additional photoexcited pair, thus separating it spatially and reducing its intensity, particularly if the charges are trapped at or near the dot surface.[31] This is true both for $S_h-S_e$ and $P_h-P_e$ photoexcited pairs. Thus, Coulomb-induced intensity attenuation (and not just Pauli blocking) can explain the bleaching of the second transition. Therefore, the final state of the first and second transitions need not be the same, as deduced by Wehrenberg et al.[4]

Clear evidence that the second transition is $P_h \rightarrow P_e$, not $P_h \rightarrow S_e$, was given by recent tunneling spectroscopy measurements.[15] The authors first measured the single-particle hole and electron states (viz. Figure 3), finding the energetic distance for the $P_h \rightarrow P_e$ and $P_h \rightarrow S_e$ pairs. Comparing these energy differences to the absorption spectra, they found that the second absorption peak (corrected by e−h Coulomb effects) corresponds to the $P_h \rightarrow P_e$ energy difference from tunneling, whereas the $P_h \rightarrow S_e$ energy difference from tunneling is a few hundreds of a millielectronvolt lower than the second absorption peak. Clearly, the second absorption peak is not due to the forbidden S−P excitation.

In summary, referring to the questions i−iii raised in the introduction, we find that (i) The band-edge states of PbSe nanocrystals evolve from the extensively split L-like VBM and CBM and partially from the Σ-like bands. The L−L splitting is caused by intervalley coupling, valence-conduction interband mixing, L-valley anisotropy and finite confining potential. (ii) The splitting of the L valley into $L_{||}$ and $L_{\perp}$ causes the isotropic $P_h \rightarrow P_e$ transition to split into $L^h_{||} \rightarrow L^e_{||}$ and $L^h_{||} \rightarrow L^e_{\perp}$. This gives rise to the $\beta$ peak corresponding to the observed second peak and the $\gamma$ peak that may be difficult to observe because of nanocrystal size dispersion. Thus, the second absorption peak is the allowed $P_h \rightarrow P_e$ transition, not the forbidden $S_h \rightarrow P_e$ (or $P_h \rightarrow S_e$) as suggested previously. The observed third peak, corresponding to the calculated $\delta$ peak, arises from two different types of symmetric transitions, $L^h_{||} \rightarrow L^e_{||}$ and $L^h_{\perp} \rightarrow L^e_{\perp}$ of a number of heavily mixed P- and D-like single-particle states. (iii) The hole levels are significantly more closely spaced than the electron levels (Figure 1) on account of L-point intervalley mixing, Σ-point contribution, and a finite confinement barrier, a finding that invalidates previous suggestions of a