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 α and β 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]