

Response Concerning “On the Interpretation of Colloidal Quantum Dot Absorption Spectra”

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In a Correspondence concerning second-derivative analysis of optical absorption spectra, Moreels and Hens use our recent paper^[1] on changes in the energy-level structure of PbSe nanocrystals as an example to discuss, as they phrase it, the pros and cons of second-derivative analysis. Two potential pitfalls are identified: i) the appearance of an artifact peak between two well-separated peaks and ii) the correct interpretation of the background in the high-energy region. Even though the Correspondence is a valid contribution to the discussion on the usefulness of second-derivative analysis, we feel that a response is appropriate since the Correspondence may give the false impression that our analysis is hampered by problems arising from the identified pitfalls.

In their Correspondence Moreels and Hens describe the problem of the appearance of an artifact peak as follows:

“However, one should be aware of artifacts. For instance, two closely spaced Gaussian peaks exhibit a second-derivative spectrum featuring three dips: two negative ones coinciding with the maxima and an additional, slightly positive dip in between. Looking at the second-derivative spectrum of the Q-PbSe absorbance shown in Figure 3, this is exactly what one gets between the first and the second absorption peak. Koole et al. suggested that this feature might be the 1S–1P optical transition. A similar dip is observable in the second-derivative spectrum of PbS Qdots (and remained unassigned). Such dips might very well be second-derivative artifacts.”

Reading the Correspondence one may think that we were not aware of this problem, and that Moreels and Hens have identified this pitfall. This is not the case. The problem is well known and in our paper we identify this problem in words very

similar to those later used by Moreels and Hens. The beginning of page 129 of our paper reads:^[1]

“Finally, one has to be aware that the second derivative itself can create artifacts. For example, the second derivative of two well-separated Gaussians has an additional minimum in between the two peaks. To analyze if the minima in the second derivative correspond to actual optical transitions, we have fitted the absorption spectrum in Figure 2A to multiple Gaussian functions. The multi-Gaussian fit of the absorption spectrum is plotted as a solid line in Figure 2A and B, and the 11 associated Gaussian functions and background function are shown as dotted lines. As can be seen in Figure 2A and B, there is an excellent agreement between the multi-Gaussian fit and the absorption spectrum.”

Not only do we identify the (well-known) problem, we also give a solution: fitting of the original absorption spectrum to a multi-Gaussian function. A good description of the measured absorption spectrum is only obtained with 11 Gaussian peaks, including the extra peak between the two strong lower-energy absorption lines, providing additional evidence for the existence of this feature. At present, the discussion on the correct assignment of the various absorption lines for PbSe quantum dots (QDs) is still continuing and new experiments such as two-photon excitation are applied to identify weak bands (or shoulders) observed in the one-photon spectrum.^[2]

The second point of Moreels and Hens involves the background correction; it is argued that for the high-energy region (from 2.5 eV) the transitions are not affected by quantum confinement, and that the strongly increasing absorption in this region is not due to Rayleigh scattering but to an increase in the local field factor f_{LF} , which can be calculated from the wavelength-dependent dielectric response of bulk PbSe. Moreels and Hens are correct in drawing attention to the local field factor, which plays an important role in the high-energy region. Note that our analysis is limited to the lower-energy region (below 2.5 eV) while the distortion of the absorption spectrum by a strongly increasing f_{LF} occurs at energies higher than 2.5 eV (see Figure 2 in the Correspondence of Moreels and Hens).

Nevertheless, it is important to also understand the high-energy part of the absorption spectrum. This point was not addressed in our paper since it was not the focus of the paper. The Correspondence is a useful addition to better understand this part of the spectrum. The analysis by Moreels and Hens shows that a satisfactory agreement in the high-energy region (E_2 in their Figure 3) is obtained by using the wavelength-dependent values for n and k from bulk PbSe. Whether or not the high-energy transitions in PbSe QDs are affected by quantum confinement, if n and k are identical to the bulk values of PbSe in this high-energy region,^[3–5] and also how to correctly correct for local field effects,^[6–8] remain important questions. In the literature there is evidence that quantum-confinement effects play an important role throughout the entire Brillouin zone (up to 4 eV) and also influences the dielectric response (and thus n and k) in the high-energy region.^[3,4] It will be interesting to see if the analysis of more

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size-dependent optical absorption spectra of PbSe QDs in the high-energy region can provide answers to these questions, and we feel that the Correspondence of Moreels and Hens is a useful contribution to this discussion.

In conclusion, the Correspondence of Moreels and Hens does not affect the analysis or the conclusions presented in our recent paper on the energy-level structure of PbSe QDs and possibly it was not intended to do so. It does present a critical evaluation of second-derivative analysis that is partly well known but also provides new insights (and questions) on how to correctly interpret the high-energy part of QD absorption spectra.

- [1] R. Koole, G. Allan, C. Delerue, A. Meijerink, D. Vanmaekelbergh, A. J. Houtepen, *Small* **2008**, *4*, 127.
- [2] J. J. Peterson, L. Huang, C. Delerue, G. Allan, T. D. Krauss, *Nano Lett.* **2007**, *7*, 3827.
- [3] Z. Hens, D. Vanmaekelbergh, E. S. Kooij, H. Wormeester, G. Allan, C. Delerue, *Phys. Rev. Lett.* **2004**, *92*, 026808.
- [4] G. Allan, C. Delerue, *Phys. Rev. B* **2004**, *70*, 24521.
- [5] J. M. An, A. Franceschetti, S. V. Dudiy, A. Zunger, *Nano Lett.* **2006**, *6*, 2728.
- [6] H. T. Dung, L. Knoll, D.-G. Welsch, *Recent Res. Dev. Optics* **2001**, *1*, 225–264.
- [7] M. E. Crenshaw, C. M. Bowden, *Phys. Rev. Lett.* **2000**, *85*, 1851.
- [8] S. F. Wuister, C. de Mello Donegá, A. Meijerink, *J. Chem. Phys.* **2004**, *121*, 4311.

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