Materials of nanometer dimensions (Reference 1) have attracted significant attention in physics, chemistry, and biology for their unique chemical and physical properties in addition to their potential technological applications mentioned below. These capabilities are mainly due to the unusual dependence of the electronic and optical properties (such as linear and nonlinear absorption) on quantum confinement, which, for semiconductor materials, restricts the particle size in the 1 to 10 nm range.

In particular, semiconductor quantum dots (QDs) have many desirable properties that are well suited for nonlinear materials, lasers, detectors, imaging agents, solar energy conversion and biomedical diagnostics. Amongst the many types of QDs are those made of II-VI and III-V semiconductors such as, CdS, CdSe, PbS, InP, and GaAs. Majority of existing work in theoretical and numerical analysis of optical properties of QDs either neglect laser propagation effects completely or significantly simplify the propagation model, so that the resulting models perform poorly in unusual conditions.

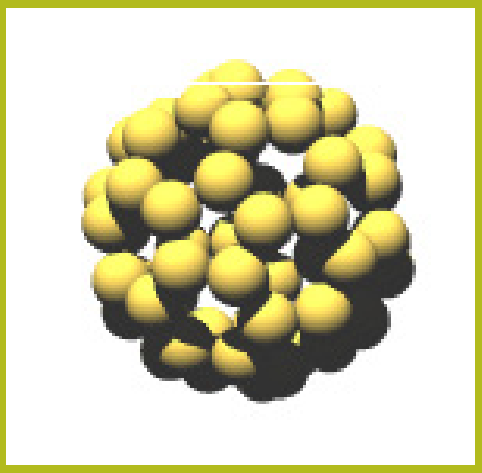
In this example we describe the incorporation of various QD absorption and relaxation mechanisms in SimphoSOFT®, which significantly enhances the QD analysis/design by enabling the user to directly calculate the laser pulse shape and electronic level populations to assess pulse distortion and intensity saturation, respectively. SimphoSOFT also includes diffraction, so that optically thick materials can be measured.

A conventional experimental method used to determine the two photon absorption in materials is the open method z-scan measurement (Reference 2). In this application note, we will describe the analysis of two-photon absorption in QD z-scan measurements using SimphoSOFT.

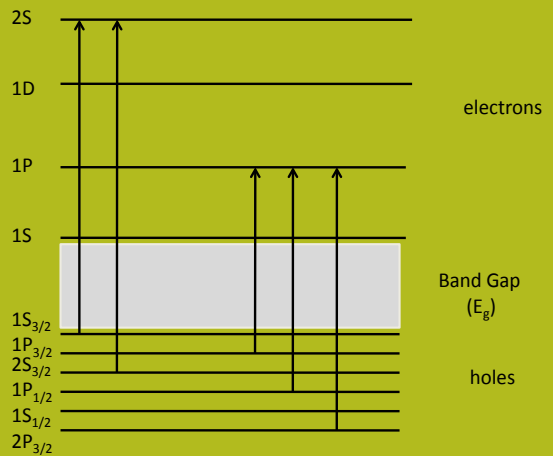
Electronic levels in semiconductor quantum dots:

A schematic diagram of a QD is given below where a group of atoms forms a nanometer sized structure. The bulk crystalline structure of the semiconductor, maintained in the QD, forms particles with atomic-like discrete energy states due to 3D confinement. Carrier dynamics in QDs are quite different from bulk materials due to the large energy level spacing and enhanced surface-to-volume ratio.

Schematic diagram of semiconductor quantum dot



Energy level diagram and transitions for semiconductor quantum dot



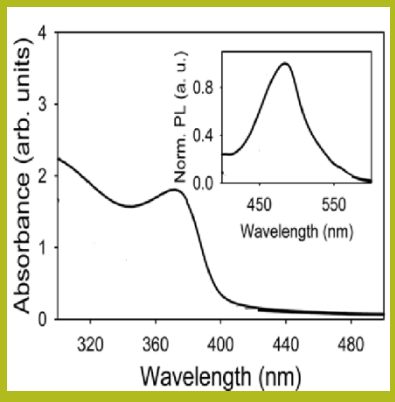
Typically the effective-mass model is used to describe the electronic structure of QDs (Reference 3). Here electron states are annotated by using a letter (l) to denote the angular momentum of the envelop wave functions. Using spectroscopic notation, the following symbols are used S for $l = 0$, P for $l = 1$, D for $l = 2$, etc. The degeneracy of the electron states are $2(2l+1)$ -fold degenerate and the lowest three electron states are denoted by 1S, 1P, 1D. The hole states are labeled similarly to electron states with an additional subscript for the total hole angular momentum (j), which have a degeneracy of $2j+1$. The first three hole states are $1S_{3/2}$, $1P_{3/2}$, and $2S_{3/2}$. The interband selection rules allow for transitions from nS_j(h) hole states to all S(e) electron states, nP_j(h) hole states to all P(e) electron states, etc. where n is the ordinal number of the level.

The above figure (right side) shows five absorptive transitions of a single photon from states $1S_{3/2}$ to 2S; $2S_{3/2}$ to 2S; $1P_{3/2}$ to 1P; $1P_{1/2}$ to 1P and $1S_{1/2}$ to 1P, which leave holes at the transitions' origins. The energies of the exciton transitions may be obtained from spectroscopic measurements.

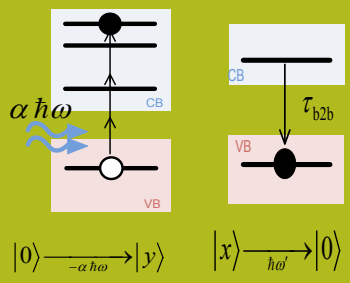
SimphoSOFT simulates photo-physical properties of QDs:

Many photo-physical QD transitions can be mapped to the existing set of SimphoSOFT transition modules, which are computational building blocks[1]. In this example, we use our multi-photon absorption transition module (TM-MPA) to model exciton formation (right image of Figure below), which excites the negatively charged electron to the conduction band, leaving a positively-charged hole in the valence band. And we use our relaxation transition module (TM-R) to model interband recombination of electron with its hole by emitting a photon (right image of figure below).

Absorption and emission spectra of QD in thin film.



Simphotek's transition module diagram for QDs. The diagram is for n-photon absorption. While n could be arbitrary, here n=2.



(Reference 4)

The absorption and emission spectra (left image of Figure above) show the linear absorption/emission occurs at about 370nm/460nm. This represents a single photon absorption/emission between the conduction/valence bands. However, measurements of the two-photon absorption coefficient require an intense laser experiment, such as the z-

[1] For modeling more extensive set of QDs transitions, including, but not limited to, single and multi-photon absorption and emission, excited state absorption, carrier multiplication, impact ionization, Auger recombination, please, contact Simphotek R&D team at support@simphotek.com.

scan method described below. Finally, the resulting SimphoSOFT energy level diagram (M-CAD) for two-photon absorption in QD is shown on the right of the figure below.

Screenshot of SimphoSOFT® M-CAD
for two-photon absorption in QDs.

Two-photon absorption (TPA) cross-section in the example 2-level model: 4.4×10^{-17} cm^4 / GW from S(0) to S(1) (References 1,2)
Relaxation time: 1 ps from S(1) to S(0).

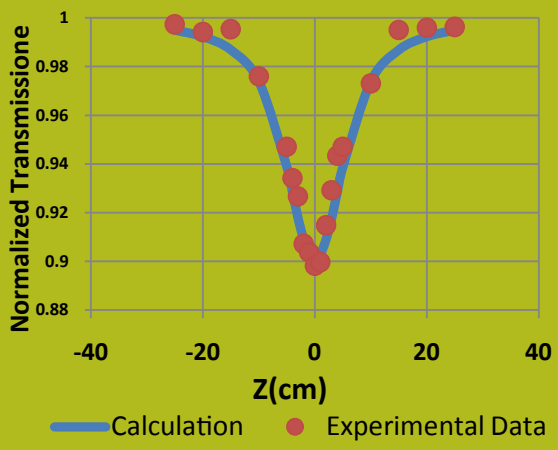
Example SimphoSOFT simulation of QDs in z-scan experiment:

Sample properties	
Molecular dopant density (concentration) in the host material	5.0×10^{18} cm^{-3}
Host material linear absorption	$\alpha = 157$ cm^{-1}
Sample length	3.7×10^{-4} cm

Laser properties	
Pulse energy	22.6 μJ
I_{00} (intensity at z=0)	3.5 GW / cm^2
w_0 (beam waist at z=0)	85 μm
Pulse FWHM	25 ps
Wavelength	532 nm
$w_0 = \pi(w_0)^2 / \lambda$	4.26 cm

The z-scan measurement is performed by moving the material in and out of the focal plane of a laser source and detecting the transmitted energy. This process can be simulated in SimphoSOFT by modulating beam waist and input intensity according to the following formulae $w^2(z) = (w_0)^2/(1 + z^2/(z_0)^2)$ and $I_0(z) = I_{00}/(1 + z^2/(z_0)^2)$. The resultant data (red dots) shown below are calculated using SimphoSOFT (blue line) to obtain the two-photon absorption coefficient.

Comparison of experiment and SimphoSOFT calculation.

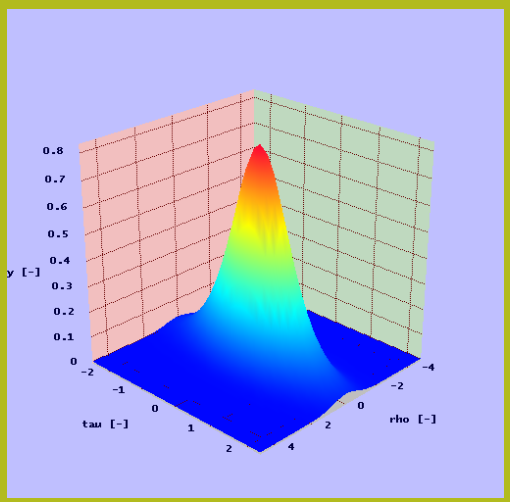


Our SimphoSOFT calculation gives a two-photon absorption coefficient 220 cm^2/GW in agreement with standard analytic equations (Reference 2).

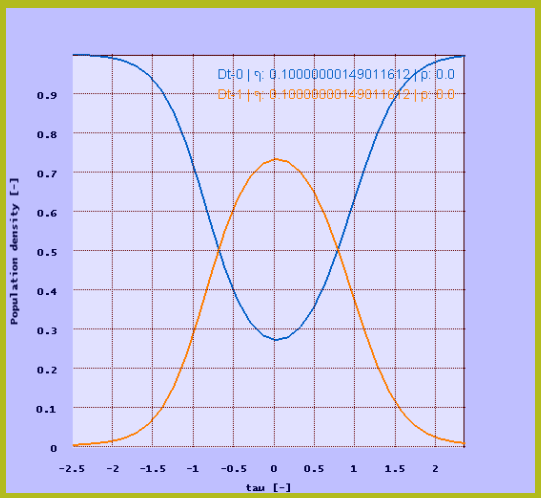
Example SimphoSOFT simulation of QDs in z-scan experiment:

In addition to determining the two photon absorption coefficient, SimphoSOFT provides information that cannot be obtained by traditional analysis. SimphoSOFT calculates the population density for all energy levels and the laser pulse shape as a function of radius and time at every location along the experimental path. For this example a decay time of 1ps was used; however, faster decay times showed no change in transmission.

The laser intensity as a function of both time and radius at the focal point.



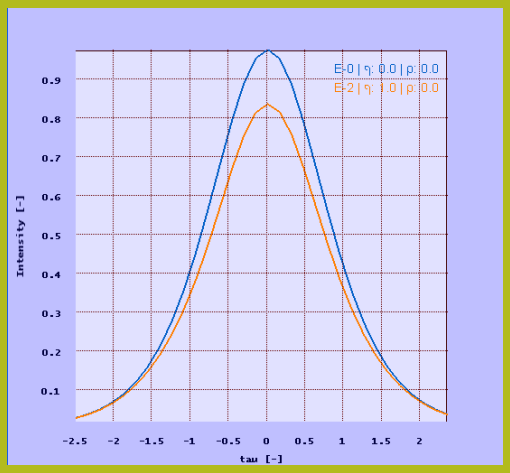
The population density as a function of time at the focal point. The blue line is the ground state and the orange line is the excited state.



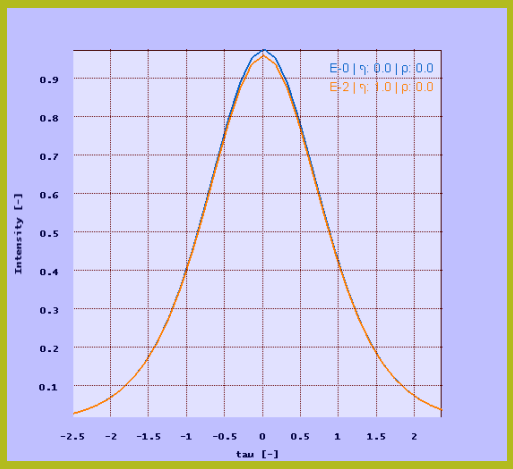
The Figure on the right shows that about 70% of the electron population is in the conduction band and 30% is in the valence band. The above problem is for inter-band transitions, but SimphoSOFT can also do intra-band transitions and transitions to impurity states in the band gap.

Two dimensional plots of the normalized intensity as a function of time are shown below. The blue (orange) curve corresponds to the input (output) of the material. These plots enable the user to determine if the laser pulse envelope is being distorted as it traverses the material.

The decrease in the intensity (orange) due to two photon absorption for I = 3.5 GW/cm^2.



When intensity I = 0.107 GW/cm^2, beam waist = 485.87μm, there is little difference between the input (blue) and the output (orange).



In this example Figures confirm that there is no pulse shape distortion in the material. The curves on the left are for relatively high intensity (3.5 GW/cm^2) and show the depletion in the laser intensity due to the two-photon absorption. The curves on the right correspond to low incident intensity (0.107 GW/cm^2) and show that there is almost no absorption as expected, i.e. the blue and orange lines overlap.

References:
(1) L. E. Brus, J. Chem. Phys. 80, 4403 (1982).
(2) M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, and E.W. Van Stryland, IEEE J. Quantum Electron. 26, 760 (1990)
(3) Al. Efros and M. Rosen, Annu. Rev. Mater. Sci. 30, 475 (2000)
(4) E. Parilov and M. Potasek, US Patent 7,949,480 B2