

# Auger Recombination in Semiconductor Quantum Dots



## ABSTRACT

We have developed analytical methods for calculating the Auger rate of recombination of excitons in bulk semiconductor and quantum dots (QDs). Using these methods we have recovered known bulk results and also obtained new results for quantum wells and wires. Recent experiments predict an inverse volume dependence in QDs different from the inverse volume-squared calculated and observed in the bulk, but as of now there is no theoretical treatment as to why this is so. Our work has shown the difficulty in dealing with the quantum confinement limit, which introduces discrete energy levels that require energy relaxation. We find that the simplest models that do not explicitly include electron-phonon interaction and impurities cannot account for the observed volume dependence.

## INTRODUCTION

A quantum dot (QD) is a nanometer-sized piece of material, usually a semiconductor, with unique electronic and optical properties. Typical sizes of QDs are 2-10 nm in diameter, containing 100-10,000 atoms. They have few conduction electrons and the reduced size leads to quantum confinement and the appearance of atom-like energy levels as shown in Figure 1.

Semiconductor QDs have been researched extensively for their applications in lasers and solar cells. The advantageous properties of QDs over bulk semiconductor materials include a "tunable" bandgap energy [1], and a high carrier density resulting in multiexciton production from a single photon [2]. The former allows lasers to emit at specifiable wavelengths (see Figure 2), and the latter the construction of extremely efficient solar cells.

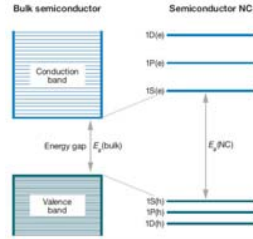
The pathway of recombination of holes and electrons (excitons) has, in particular, attracted a lot of attention. Experimental evidence [3] shows that nonradiative Auger recombination is the dominant mechanism of electron relaxation. Auger recombination (illustrated in Figure 3) occurs when an exciton recombines and instead of emitting light, transfers the energy to a nearby electron (or hole), creating a "hot" electron (hole). In QD lasers, nonradiative processes are to be minimized, while in PV cells, exciton recombination detracts from the overall quantum yield. Hence, an accurate description of the relaxation time (the inverse of recombination rate) is essential to increasing the effectiveness of QDs.

We present a derivation that obtains agreement with the known bulk rate and modify it to account for the discrete atom-like energy levels in the QD.



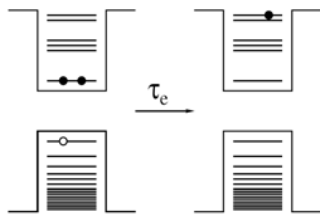
**Figure 2.** CdSe QDs of different sizes can fine-tune optical absorption properties.

Source: Andrey Rogach. Available at: [www.nanopichoftheday.org/2003Pic/QRainbow.htm](http://www.nanopichoftheday.org/2003Pic/QRainbow.htm)



**Figure 1.** Continuous energy levels in bulk (left) give way to discrete energy levels in QDs (right).

Source: V. Klimov, *Annu. Rev. Phys. Chem.* **58**, 635 (2007)



**Figure 3.** Auger recombination schematically in terms of energy bands. Two electrons and a hole (left) recombine to form a "hot" electron (right), with time constant  $\tau_c$ .

Source: L. W. Wang, M. Califano, A. Zunger, A. Franceschetti, *Phys. Rev. Lett.* **91**, 056404 (2003).

## References

- [1] "Spectral and Dynamical Properties of Multiexcitons in Semiconductor Nanocrystals." V. Klimov, *Annu. Rev. Phys. Chem.* **58**, 635 (2007).
- [2] "High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion." R. D. Schaller and V. I. Klimov, *Phys. Rev. Lett.* **92**, 186601 (2004).
- [3] "Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots." V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale, M. G. Bawendi, *Science*, **287**, 1011 (2000).
- [4] "Pseudopotential Theory of Auger Processes in CdSe Quantum Dots." L. W. Wang, M. Califano, A. Zunger, A. Franceschetti, *Phys. Rev. Lett.* **91**, 056404 (2003).
- [5] "The Case for Auger Recombination in In(1-x)Ga(x)As(1-y)V(y)." N. K. Dutta and R. J. Nelson, *J. Appl. Phys.* **53**, 74 (1982).

Eq. 1: Bulk

$$\frac{R_{total}}{vol} \propto n_e^2 n_h \frac{L_T^3}{E_g \sqrt{m_e E_g}} e^{-\beta E_g \frac{\mu}{\mu+1}}$$

Eq. 2: Well

$$\frac{R_{total}}{vol} \propto n_e^2 n_h W \frac{L_T^2}{E_g \sqrt{m_e E_g}} e^{-\beta E_g \frac{\mu}{\mu+1}}$$

Eq. 3: Calculated QD

$$\frac{R_{total}}{vol} \propto \frac{\Lambda}{E_g^2 + \Lambda^2} \frac{1}{(vol)^{5/3}}$$

Eq. 4: Rate volume dependencies

$$\frac{R_{QD,calculated}}{vol}^{-2/3} > \frac{R_{QD,experimental}}{vol}^{-1} > \frac{R_{bulk}}{vol}^{-2}$$

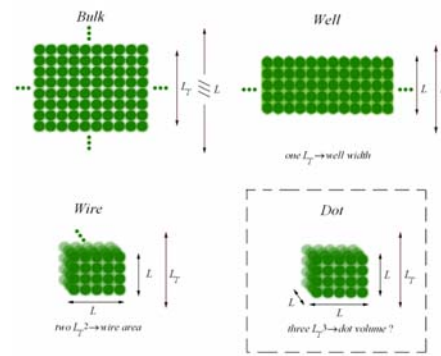
**Eqns 1-4.** Auger rates per volume in bulk (1), well (2), and QD (3); volume dependence comparison for calculated QD, experimental QD and bulk (4). Here,  $L_T$  is the temperature length;  $\Lambda$  is an energy conservation broadening parameter;  $E_g$  is the bandgap energy;  $n_{e/h}$  is electron/hole density;  $m_e$  is the electron mass; and  $\mu$  is the ratio of electron to hole effective masses.

## Derivation of Rate in Bulk

We used second-quantized methods to write the interaction operator and solved for the transition matrix element assuming Bloch wave-functions (valid for crystals sufficiently many atoms across). Using Fermi's Golden Rule we then obtained a rate expression in terms of a sum over initial and final wave-vectors of these matrix elements and occupation probabilities (given by Boltzmann statistics; valid in this exponentially prohibited reaction) with a delta function enforcing energy conservation. The sum can be converted to an integral and evaluated using saddle point methods, and gives the correct size and exponential temperature dependence (Eq. 1).

## Introducing Confined Dimensions

The quantum well (2-D) and quantum wire (1-D) are easier to tackle than the QD (0-D), where (n-D) is the number of free dimensions with effectively continuous energy levels. We followed a similar derivation to the above except for the quantum-confined dimensions; we handled these by leaving it in sum form and after taking into account energy



**Figure 4.** Length scales governing quantum confinement:  $L_T$  is the temperature length and  $L$  is the physical size. The dot result is an extrapolation, not the result of a derivation.

## METHOD

conservation, we replace temperature length(s) by a physical length, either the well width (Eq. 2) or the wire cross-sectional area.

## Quantum Dot Rate

It has been postulated that the exciton pair immediately relaxes to its first excited state before undergoing Auger recombination. Therefore, we take the probability of occupation to be 1 for lowest-lying states and 0 otherwise. We also assume that the length scale corresponding to the bandgap energy is much less than the size of the dot given that typical bandgap energies correspond to Angstrom length scales and typical QDs have sizes of greater than a few nanometers. With carrier kinetic energies much less than the required bandgap energy, we must broaden the energy conservation delta function. In practice, this amounts to taking into account energy relaxation through dissipation. We use a Lorentzian [cf. Ref. 4] with a characteristic energy scale  $\Lambda$ , leading to the rate in Eq. 3.

## ANALYSIS

Our results for the well and wire show an interesting trend: when a physical dimension becomes comparable with the temperature length, we replace  $L_T$  by  $L$ , the constrained dimension. In Figure 4, we show the length scales in question and a QD extrapolation.

A comparison of the calculated and the observed QD rate along with the known bulk rate is shown in Eq. 4. The derived bulk rate gives the correct size dependence, but the experimental rate determined by Klimov et al. [3] does not fit with our result and instead lies between our QD and the bulk rate. There are two possibilities for this that we put forward. One is that the actual behavior, assumed in Ref. 3 to be an exact inverse volume proportionality could be a mixture of (size-constrained) and (bulk-like) effects. Further calculations of the relative contributions of these two rates is called for and beyond the scope of this study.

The other more likely scenario is that the model we have presented, which neither explicitly includes phonon-electron interaction nor the increased electron-electron wave function overlap is too simple to account for the size-dependence in the QD. Using naively the same reasoning for the QD as for the well and wire we would expect an extra factor of volume, giving us the correct size dependence (as shown in the dotted box of Fig. 4); however, this fails to take into account energy conservation broadening and hence is difficult to justify. Carrier trapping leading to broadened momentum conservation has also been analyzed in Ref. 5 and could lead to a different size dependence. In addition there are several length scales in the problem, the size of the QD, the temperature length, the bandgap energy length, and the Lorentzian length scale. Thus there are a number of regimes with different volume dependencies and crossovers that complicate the comparison to experiment.

## DISCUSSION

The expressions we derived provide a sound starting point for further calculations of Auger rates. We have shown the method to be valid by obtaining good agreement with the theoretically known rate in bulk semiconductor. The extrapolation of this method to the QD has given a different size dependence from that experimentally determined, and indicates that new physics must be introduced.

## ACKNOWLEDGEMENTS

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