`LumiTrans`: a computer program to fit luminescence decay curves

Juan Manuel Castillo Sanchez[1], Thijs J.H. Vlugt[1], Andries Meijerink[2]

[1]Process & Energy Laboratory, Delft University of Technology,
Leeghwaterstraat 44, 2628 CA Delft, The Netherlands
[2]Condensed Matter and Interfaces, Department of Chemistry,
Utrecht University, P.O. Box 80.000, 3508 TA Utrecht,
The Netherlands

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1   Introduction

This document describes how to use the computer program `LumiTrans`. The methodology is briefly summarized, for a detailed description the reader is referred to Ref. [1]. An example of how to use the program is given below.

2   Theory

Research on quantum cutting systems is nowadays focused on combinations of ion types. In such a system, the energy of a central atom (also called donor) is transferred to one or two acceptor ions. This process is generally known as downconversion. The computer program `LumiTrans` can be used to compute luminescence decay curves of a donor-acceptor system embedded in a host lattice. It can account for a direct energy transfer, a cooperative mechanism and an accretive mechanism. The interactions can be modeled using dipole-dipole (r^{-6}), dipole-quadrupole (r^{-8}) or quadrupole-quadrupole (r^{-10}) interactions.

In the program, we need to define a host lattice for incorporating the donor and acceptor ions. We assume that the ions of the host lattice do not influence the transfer process. It is possible to define your own lattice structure. The following lattices have already been predefined: LaF_3, LiF_4, YF_3, YPO_4. We assume that the donor is present in very low concentrations so that in a user-defined supercell only a single donor atom is present. The concentration of the acceptor ion can be varied (in the program, `% of active sites`). The concentration of acceptor ions can be set to zero, and in this case it is not necessary to specify the mechanism and the interaction. We assume that the donor and acceptor ions are

randomly distributed over the lattice. For a *single* realization of the donor and acceptor ions, the decay curve is given by a (single) exponential decay

$$I(t) = \exp[-t(G_{\text{rad}} + G_{\text{tr}})] \tag{1}$$

in which t is time, G_{rad} is the radiative decay rate and G_{tr} is the energy transfer rate. The value of G_{rad} is usually constant for a given donor, while the transfer rate G_{tr} depends on the precise positions of the donor and acceptor ions. The signal measured in decay experiments can be considered as an ensemble average over all possible realizations of the positions of the donor and acceptor ions (we assume that these ions are randomly distributed)

$$\langle I(t) \rangle = \langle \exp[-t(G_{\text{rad}} + G_{\text{tr}})] \rangle \tag{2}$$

In the computer program, K random realizations are generated (in the program: `# of configurations`) and the average decay is computed using

$$\langle I(t) \rangle \approx \frac{\sum_{i=1}^{K} \exp[-t(G_{\text{rad}} + G_{\text{tr}}(i))]}{K} \tag{3}$$

in which $G_{\text{tr}}(i)$ is the transfer rate corresponding to realization i. In practice, $K = 2 \times 10^4$ random realizations of the donor/acceptor ions are usually sufficient. The larger the number of random realizations, the better the fitting will be and the longer the calculation will take. In addition, there is one point where a further increase of this value does not provide a significant enhancement of the result. For a particular transfer mechanism, the transfer rate G_{tr} for a certain realization of the ions can be computed as follows:

$$\text{Single} - \text{transfer}: \quad G_{\text{tr}} = C \sum_{i=1}^{N} \frac{1}{r_{id}^{\alpha}} \tag{4}$$

$$\text{Cooperative}: \quad G_{\text{tr}} = C \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{r_{id}^{\alpha} r_{jd}^{\alpha}} \tag{5}$$

$$\text{Accretive}: \quad G_{\text{tr}} = C \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \left(\frac{1}{r_{id}^{\alpha} r_{ij}^{\alpha}} + \frac{1}{r_{jd}^{\alpha} r_{ij}^{\alpha}} \right) \tag{6}$$

in which C is a constant (that can be fitted to match experimental decay curves), N is the number of acceptor ions in the system, r_{ij} is the distance between acceptor ions i and j, and r_{id} is the distance between the donor ion and acceptor ion i. The power α determines the type of interaction: dipole-dipole ($\alpha = 6$), dipole-quadrupole ($\alpha = 8$) or quadrupole-quadrupole ($\alpha = 10$). In the summations over all acceptor ions in the system, we take the nearest image convention into account for systems with periodic boundary conditions [2, 3].

3　Example

As an example, consider the system YF_3:Nd^{3+},Yb^{3+}. This means that the host lattice is YF_3, Nd^{3+} is the donor and Yb^{3+} is the acceptor. The characteristics of this system are described in detail in Ref. [4]. In the directory `ExperimentalDecayCurves`, the experimental decay curves for 0%, 2% and 5% Yb^{3+} are given (normalized intensity, time in ms). Using the experimental decay curve for the system without Yb^{3+}, the only mechanism is radiative decay (single-exponential decay) and we find a radiative decay rate of $G_{rad} = 0.0025$ ms^{-1}. Using this value for G_{rad}, we can fit the value of C at a concentration of 2% Yb^{3+}, assuming either a cooperative or a single transfer mechanism. For this, the following settings can be used: `# of configurations` equals `20000`, `% active sites` equals `2`, `Timestep` equals `0.2` (note: here in units of ms as G_{rad} was set in units of ms^{-1}) and `Number of bins` equals `5000`. The number of bins specify the number of time steps we take, so the total time in the simulation will be equal to the time step multiplied by the number of bins. When you provide an experimental curve for fitting, the first values of the curve are usually disregarded because they just contain noise or data obtained during equilibration or calibration. With the parameter `Time origin`, all the data points of the experimental curve which time is lower than this value are disregarded, and the time origin (time=0 seconds) is set at that point. For the experimental curves provided with the program, the time origin should be set to zero. You can provide initial guess values of G_{rad} and C in the `Grad` and `C` fields respectively. If these fields are left blank, the program will generate initial guess values randomly. At the end of the calculation, the final value of every fitted parameter will be filled in its corresponding field. It is possible that at the end of the simulation you do not obtain good fitting parameters. One possible reason can be that the simulation did not have time to converge, for example because you used too few configurations in the field `# of configurations`. In this case, the best thing you can do is running again the program using the final fitting parameters obtained in the previous simulation as starting guess values for the new simulation. This can be achieved simply clicking the `Run` button again without changing any parameter.

We assume a dipole-dipole transfer ($\alpha = 6$). For the single-transfer mechanism we find $C \approx 720\,\mathrm{ms}^{-1}\mathrm{\AA}^6$ and for the cooperative mechanism $C \approx 7.8 \times 10^8\,\mathrm{ms}^{-1}\mathrm{\AA}^{12}$. These values can be used to predict the decay curves for 5% Yb^{3+}. You can check for yourself that the single transfer mechanism nicely describes the experimental data for 5% Yb^{3+} using $C = 720\,\mathrm{ms}^{-1}\mathrm{\AA}^6$. The coorperative and accretive mechanism fail to describe the experimental data for 5% Yb^{3+} using the value of C fitted for 2% Yb^{3+}, strongly suggesting that these processes do not take place here.

References

[1] Vergeer, P., Vlugt, T.J.H., Kox, M.H.F., den Hertog, M.I., van der Eerden, J.P.J.M., and Meijerink, A. (2005). "Quantum Cutting by Cooperative Energy Transfer in $Yb_xY_{(1-x)}PO_4$:Tb^{3+}", *Phys. Rev. B*, **71**, 0141119.

[2] Allen, M.P. and Tildesley, D.J. *Computer Simulation of Liquids*. Clarendon Press, Oxford, 1987.

[3] Frenkel, D. and Smit, B. *Understanding Molecular Simulation: from Algorithms to Applications*. Academic Press, San Diego, 2nd edition, 2002.

[4] Aarts, L., Meijer, J.M., van der Ende, B.M., Vlugt, T.J.H., and Meijerink, A. (2009). "Downconversion for solar cells in YF_3:Nd^{3+},Yb^{3+}", *Phys. Rev. B*, **81**, 035107.