A Multi-Scale Approach to Simulate Molecules in Complex Photonic Devices

Benedikt Zerulla,[1,*] Marjan Krstić,[2] Dominik Beutel,[2] Christof Holzer,[2] Christof Wöll,[3] Carsten Rockstuhl,[1,2] and Ivan Fernandez-Corbaton[1]

[1] *Institute of Nanotechnology, Karlsruhe Institute of Technology, D-76344 Eggenstein-Leopoldshafen, Germany*
[2] *Institute of Theoretical Solid State Physics, Karlsruhe Institute of Technology, D-76131 Karlsruhe, Germany*
[3] *Institute of Functional Interfaces, Karlsruhe Institute of Technology, D-76344 Eggenstein-Leopoldshafen, Germany*

[*] *benedikt.zerulla@kit.edu*

Abstract: We present a novel multi-scale approach for obtaining the optical response of molecular structures inside photonic devices from first principles. The approach combines quantum-chemical computations with rigorous Maxwell solvers.

1. Introduction

The development of fabrication techniques that aim at providing artificial materials with on demand optical properties has shown significant progress in recent years. A notable class of specifically designed materials are molecular materials thanks to their larger design space and the wide range of properties that can be tailored. To interpret experimental measurements and predict material properties beforehand, accurate and efficient theoretical models are essential. The computational challenge in such systems is the presence of critical dimensions across multiple length scales, ranging from the size of a single molecule (ångströms) to the size of the photonic device ((milli)meters). To entirely accommodate those length scales, we present a novel multi-scale approach to simulate various configurations of molecules in complex photonic devices. Our approach incorporates the properties of the individual molecular unit and its interaction with multiple molecules in spatially extended complex photonic devices. It is perfectly suitable for predicting many experimentally observable properties.

Our multi-scale approach is based on the transition matrix (T-matrix), which is suitable for describing the optical scattering properties of a finite number of either artificial or natural scatterers, as in this contribution. The method starts by computing the T-matrix of an individual molecule using quantum-chemical methods, which allows to consider it afterward just like any other scatterer in a traditional Maxwell-solver. As a proof-of-concept, a surface-anchored metal-organic framework (SURMOF) inside an optical cavity is analyzed.

2. T-matrix Formalism

The T-matrix $\mathbf{T}$ relates the multipolar expansions of the scattered and incident fields for a scattering object [1]. The dipolar T-matrix with blocks $\mathbf{T}_{ij}$, $i,j = \mathrm{N},\mathrm{M}$, can be derived from dipolar polarizability tensors as [2]:

$$\begin{pmatrix} \mathbf{T}_{\mathrm{NN}} & \mathbf{T}_{\mathrm{NM}} \\ \mathbf{T}_{\mathrm{MN}} & \mathbf{T}_{\mathrm{MM}} \end{pmatrix} = \frac{\mathrm{i}c_\mathrm{h}Z_\mathrm{h}k_\mathrm{h}^3}{6\pi} \begin{pmatrix} \mathbf{C}\,(\boldsymbol{\alpha}_{\mathrm{ee}})\,\mathbf{C}^{-1} & \mathbf{C}\,(-\mathrm{i}\boldsymbol{\alpha}_{\mathrm{em}}/Z_\mathrm{h})\,\mathbf{C}^{-1} \\ \mathbf{C}\,(\mathrm{i}\boldsymbol{\alpha}_{\mathrm{me}}/c_\mathrm{h})\,\mathbf{C}^{-1} & \mathbf{C}\,(\boldsymbol{\alpha}_{\mathrm{mm}}/(c_\mathrm{h}Z_\mathrm{h}))\,\mathbf{C}^{-1} \end{pmatrix}. \tag{1}$$

$c_\mathrm{h} = 1/\sqrt{\varepsilon_\mathrm{h}\mu_\mathrm{h}}$ is the speed of light in the host medium, $Z_\mathrm{h} = \sqrt{\mu_\mathrm{h}/\varepsilon_\mathrm{h}}$ its impedance, and $k_\mathrm{h} = \omega\sqrt{\varepsilon_\mathrm{h}\mu_\mathrm{h}}$ is the wave number with ε_h the permittivity and μ_h the permeability of the host medium. $\mathbf{C}$ are matrices transforming the polarizabilities from the Cartesian to the spherical basis. The dipolar polarizability tensors are calculated using time-dependent density functional theory (TD-DFT). To describe the interaction of a molecule with other molecules in a two-dimensional lattice with lattice vectors $\boldsymbol{R}$, the effective T-matrix is computed [3],

$$\mathbf{T}_{\mathrm{eff}} = \left(\mathbf{I} - \mathbf{T} \sum_{\boldsymbol{R}\neq 0} \mathbf{C}^{(3)}(-\boldsymbol{R})\mathrm{e}^{\mathrm{i}\boldsymbol{k}R} \right)^{-1} \mathbf{T}, \tag{2}$$

which describes the scattering from the object inside the lattice. $\boldsymbol{k}$ is the incident wave vector and $\mathbf{C}^{(3)}(-R)$ are matrices translating the scattered fields of the other scatterers in the lattice to the origin. To simulate quantities such as absorption and circular dichroism of a macroscopic device consisting of a three-dimensional lattice of molecules, the response of several stacked lattices is combined. Here, a combination with slabs is possible enabling the simulation of filled cavities, for instance. To simulate the response of molecules structured in specific shapes such as cylinders or spheres, one can calculate their effective material parameters. With the calculated effective material parameters, solutions for arbitrary shapes can be obtained with finite-element method based solvers [5].

3. Coupling of a SURMOF and an Optical Cavity

To demonstrate the strength of our multi-scale approach, we consider a Zn-SiPc-SURMOF-2 inside an optical cavity formed by two silver mirrors [4]. A SURMOF consists of metal ions connected by photoactive organic linker molecules, grown in a crystalline manner on a substrate. First, the T-matrices of a unit cell of the SURMOF are calculated using TD-DFT. Then, the response of the stacked lattices in vacuum and of the illuminated filled cavity is calculated. In Fig. 1**(a)**, the absorption of the SURMOF in vacuum is shown for different frequencies of the incident light and different values of the thickness of the SURMOF film. In Fig. 1**(b),(c)**, we show the calculated refractive index of the SURMOF together with the cavity modes. The filled cavity shows regions of high absorption, which are bent close to the frequency ranges for which the absorption of the bare SURMOF is high. These regions of high absorption of the filled cavity are cavity modes, which are bent due to the coupling to the SURMOF resonances. In Ref. [6], the filled cavity has been analyzed for a film thickness of 400 nm. By comparing to the simulated spectra, we deduce that the two peaks of the absorption measured in the experiment belong to two different cavity modes and not to a lower and upper polariton branch. This is due to the highly dispersive refractive index of the SURMOF, which changes significantly from the frequencies below and above the resonances of the SURMOF. In Ref. [4], it is additionally shown that for a mixture of J-aggregates in a polymer such a result is not observed, as they are not as densely packed as the SURMOF, leading to a less dispersive refractive index. For the SURMOF, the length of the linker molecules can be increased to decrease the refractive index. This example demonstrates that our multi-scale approach can be, first, used to explain and interpret experimental measurements in more detail, and, second, to suggest alternative structures and designs for specific applications.

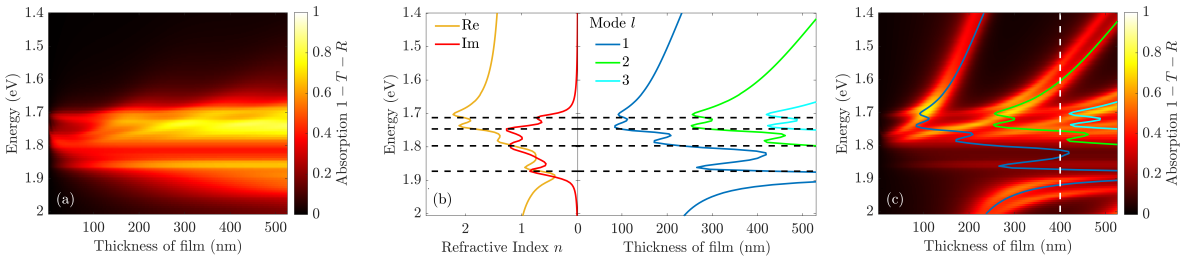

Fig. 1: Absorption of surface-anchored metal-organic framework (SURMOF) Zn-SiPc-SURMOF-2 in vacuum **(a)**, refractive index of the SURMOF and cavity modes of optical cavity filled with SURMOF **(b,c)**. The cavity modes are bent due to the coupling to the SURMOF resonances. Modified images from Ref. [4].

4. Conclusion

We have presented a novel multi-scale approach to simulate optical devices consisting of molecules and photonic elements. The optical properties of a unit of the molecular structure are calculated using time-dependent density functional theory, and the response of the macroscopic molecular system integrated into a complex environment is calculated afterward using a T-matrix approach. We applied the multi-scale approach to the example of a surface-anchored metal-organic framework inside an optical cavity. At the conference, the large predictive power of our novel workflow is presented for designing new devices with tailored chiral and nonlinear optical properties.

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