How can (TD-)DFT improve multi-scale optical simulations of novel nano-materials and devices?

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Abstract: T-matrices of molecular materials, expressing their scattering properties, can be constructed from precise quantum-chemical calculations, enabling the use of efficient Maxwell solvers for multi-scale simulations of optical devices built from new materials.

1. Introduction

The explosion of novel approaches aiming at the fabrication of materials with on-demand properties, and advances in engineering techniques accelerated the development of optical devices covering the size scales from nanometers to meters. Designing new or improving the performance of existing optical devices requires the interplay among multiple scientific fields such as (quantum) chemistry, physics (optics), and material science combined with engineering skills. However, adapted theoretical methods able to bridge scales from atomistic (Ångströms) to device levels (µm - m) are yet scarce. Particularly challenging is the construction of transition matrices (T-matrices) for novel materials for which effective parameters cannot be obtained experimentally. The importance derives from the opportunity to couple nowadays precise molecular quantum-chemical calculations of materials with Maxwell solvers through the T-matrix of the material which can then be used to build more complex optical devices. [1]

In this contribution, a bottom-up workflow based on the (time-dependent) density functional theory ((TD-)DFT) is introduced, allowing us to study light-matter interactions at the quantum level and to construct T-matrices for molecular materials, such as surface-grown metal-organic frameworks (SURMOF). These constructed T-matrices can be used in multi-scale simulations of novel optical devices through digital twins.

2. Methodology

The workflow to calculate first-principle T-matrices of molecular materials (Fig. 1) consists of: i) Optimization of a single molecule or the unit cell of the crystalline material. ii) Choosing a suitable finite-size model to capture all important optical interactions. iii) Simulation of the spectra to determine the spectral range and understand the origin of spectral features using TD-DFT approach. iv) Calculation of electric-electric, electric-magnetic, and magnetic-magnetic dynamic polarizabilities in dipole approximation for discrete frequencies in a given frequency range. v) Construction of T-matrices from calculated polarizabilities according to theory presented in [1, 2].

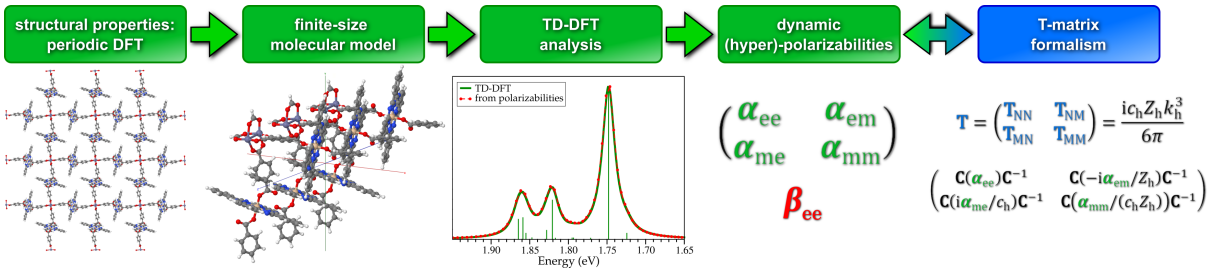

Fig. 1: Workflow for the T-matrix construction of novel materials such as SURMOFs. Adapted from [2]

Additionally, it is also possible to calculate electric-electric first hyper-polarizabilities for nonlinear optics in step iv) if those are at stake. Finally, T-matrices obtained for novel molecular materials from quantum chemistry simulations can be used to retrieve homogeneous effective material parameters. [3]

3. Results

The described workflow was applied to study the optical properties and construct T-matrices of three different MOF materials. MOFs are an artificial class of hybrid materials made by arranging metal and organic building blocks in periodic crystalline scaffolds. By selection of optically active organic molecules to connect metallic centers, MOFs with a tailored optical responses are prepared. DFT allows us to study UV-VIS absorption, electronic circular dichroism (ECD), infra-red (IR) absorption, and vibrational circular dichroism (VCD) of such materials.

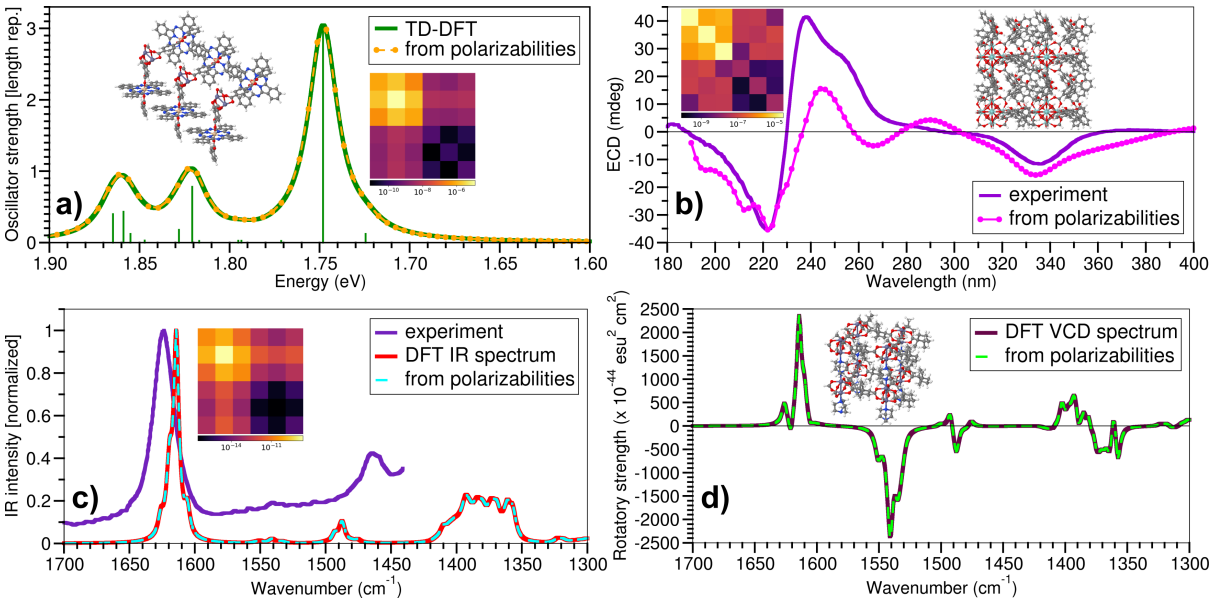

Fig. 2: Optical properties of SURMOFs: a) Absorption of Zn-SiPc-SURMOF-2 from dynamic polarizabilities matches the one obtained from the discrete electronic excitations. The T-matrix is visualized at 1.748 eV. [2] b) ECD spectrum from polarizabilities of chiral UiO-67-BINOL SURMOF and comparison with the experiment. T-matrix is at 222 nm. c) IR spectrum (T-matrix is at 1615 cm^{-1}, exp. IR adapted from: Gu *et al.*, *Chem. Eur. J.* 2014, 20, 9879) and d) VCD spectrum of the Zn-L-camphoric acid-dabco SURMOF.

Figure 2 a) shows the simulated UV-VIS absorption spectra of three unit cells of Zinc-Si-Phthalocyanine MOF. We notice three characteristic peaks that were observed experimentally as well. The match between the two spectra obtained from different approaches gives confidence to proceed with constructing T-matrices. Figure 2 b) exhibits an excellent agreement between the ECD spectrum of UiO-67-BINOL MOF and experiment. Figures 2 c) and d) show vibrational IR and VCD rotatory strengths of the Zinc-camphoric acid-dabco MOF. Features of the IR spectrum are reproduced. The analysis of the vibrational modes of the molecular model offers insights into the influence of the structural features to the IR and VCD spectrum. For all MOF materials, the dipolar T-matrix is shown in the insets at the most intense resonance wavelength.

4. Conclusions

A novel first-principles based T-matrix approach to study optical processes of molecular materials has been presented for different spectroscopies. The excellent agreement between simulations and experiments for SURMOFs has also been presented. Furthermore, quantum-chemical simulations allows us to construct T-matrices of molecular materials, which can be employed in multi-scale Maxwell scattering simulations, opening a promising route for the design of novel optical devices based on new materials with unprecedented performance. In this context, further developments of methods and codes for nonlinear optical properties of materials and devices are ongoing.

References

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