QED-Chemistry and Materials: First principles modeling of Light-matter interactions within QED-TDDFT

Angel Rubio
Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany
Email: angel.rubio@mpsd.mpg.de

Computer simulations that predict the light-induced change in the physical and chemical properties of complex systems, molecules, nanostructures and solids usually ignore the quantum nature of light. Recent experiments at the interface between materials science and quantum optics have uncovered situations where both the molecular system and the photon field have to be treated in detail. In this talk, we show how theoretical approaches have to be adapted to treat such coupled matter–photon problems and which effects can be anticipated. We demonstrate how the effects of treating quantum-photons can be properly included in such calculations. Our newly developed quantum electrodynamics density-functional formalism (QED-TDDFT**)** provides this theoretical framework. The basic idea is to treat the full QED system of particles and photons as a quantum fluid. Here the particles are represented by a charge current, and the photons by a classical electromagnetic field that acts on the current in a very complex manner. We will provide an overview of how well-established concepts in the fields of quantum chemistry and material sciences have to be adapted when the quantum nature of light becomes important in correlated matter-photon problems. We analyse model systems in optical cavities, where the matter-photon interaction is considered from the weak- to the strong coupling limit and for individual photon modes as well as for the multi-mode case. We identify fundamental changes in Born-Oppenheimer surfaces, spectroscopic quantities, conical intersections and efficiency for quantum control. We apply the new quantum-electrodynamical density-functional theory to single-photon emission and show how a straightforward approximation accurately describes the correlated electron-photon dynamics.

We will also address how periodic driving of many-body systems offers a platform to design Floquet states of matter with tunable electronic properties on ultrafast time scales. Based on the previous QED-TDDFT theoretical framework, we will introduce Floquet time-dependent density functional theory (Floquet-TDDFT) as a general and robust first principles method for predictive Floquet engineering of topological states of matter. Using this scheme we show how femtosecond laser pulses with circularly polarised light can be used to switch between Weyl semimetal, Dirac semimetal, and topological insulator states in a prototypical 3D Dirac material, Na3Bi. Our findings are general and apply to any 3D Dirac semimetal. Furthermore, we show that the concepts of Floquet analysis can be applied to monitor electron photon and electron-phonon dressing in 2D materials . This coupling leads to phonon- or photon-dressed quasi-particles (polarons or polaritons) imprinting specific signatures in the spectrum of the electronic structure that can be detected by time dependent ARPES as sidebands to the equilibrium band structure. Most strikingly, we find that the non-equilibrium electronic structure created by coherent dynamical dressing is the same for photon and phonon perturbations. We demonstrate that if time-reversal symmetry is broken by the coherent lattice perturbations a topological phase transition can be induced. The extension to spin-resolved ARPES can be used to predict asymmetric dichroic response linked to the valley

selective optical excitations in monolayer transition metal dichalcogenides (TMDs). This work establishes that the recently demonstrated concept of light-induced non-equilibrium Floquet phases can also be applied when using coherent phonon modes for the dynamical control of material properties. The present results are generic for bosonic time-dependent perturbations, therefore we envision similar phenomena to be observed for example for plasmon, magnon or exciton driven materials.

The new QED-TDDFT framework introduced here paves the road to describe matter-photon interactions from first-principles and deal with emergent properties of matte, opening the possibility to predict and control the change of material properties, selectively trigger physicochemical processes, alter chemical reactions, and create new state of matter due to the interaction with light from first principles.

References:

H. Hübener, U. de Giovannini, A. Rubio, Phonon driven Floquet matter,, (2017);
H. Hübener, M. A. Sentef, U. de Giovannini, A.F. Kemper, A. Rubio, Creating stable Floquet-Weyl semimetals by laser-driving of 3D Dirac materials, Nature Communications 7, 13940 (2017)

N. Tancogne-Dejean, O. D. Mucke, F. X. Kartner , A. Rubio, Impact of the electronic band structure in high-harmonic generation spectra of solids, Physical Review Letters 118, 087403 (2017); Ellipticity dependence of high-harmonic generation in solids: unraveling the interplay between intraband and interband dynamics Nature Communications (2017)

U. De Giovannini, H. Hübener, A. Rubio, Monitoring electron-photion dressing in WSe2, NanoLetters {\bf 16} 7993–7998 (2016)

Atoms and Molecules in Cavities: From Weak to Strong Coupling in QED Chemistry, J. Flick, M. Ruggenthaler, H. Appel, A. Rubio, Proceedings of The National Academy of Sciences of The United States of America 114, 3026–3034 (2017)

Kohn-Sham Approach to Quantum Electrodynamical Density Functional Theory: Exact Time-Dependent Effective Potentials in Real Space J. Flick, M. Ruggenthaler, H. Appel, A. Rubio
Proceedings of The National Academy of Sciences of The United States of America 112 15285-15290 (2015)