

Relativistic and non-adiabatic developments for molecular quantum theory

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High and ultra-high precision spectroscopy experiments of small molecular systems make it possible to test and further develop the fundamental theory of molecular matter. The molecular and atomic range of matter is governed by quantum mechanics and the interaction of the constituent particles, the electrons and the atomic nuclei, is dominated by electromagnetic interactions. Although the Lagrangian density of relativistic quantum electrodynamics is standard textbook material, it is a non-trivial task to write down the most possible complete wave equation (that fulfills basic requirements, like Lorentz invariance) and that could be solved (numerically) to high precision. To compute bound and quasi-bound molecular states, series approximations have been traditionally evoked in terms of the small parameters of the theory: the electron-to-proton mass ratio, $(m_e/m_p)^{1/2}$, the fine-structure constant, α , and its nuclear-charge-number multiple, $Z\alpha$. The series expansions of the relativistic QED description of few-body systems lead to the fundamental concepts currently in use, e.g., the Schrödinger equation and the Born–Oppenheimer approximation to describe the structure and dynamics of molecular systems. Furthermore, the series expansions result in a number of ‘effects’ that needs to be accounted for by perturbation theory, if a quantitative theory-experiment agreement is sought for. Comparison with experiments of high energy resolution shows that the ‘small’ effects often ignored (or approximated) are ‘visible’ and important, their partial cancellation cannot be predicted *a priori*, moreover, the relative magnitude of the corrections changes from system to system and from transition to transition. Although the perturbative non-adiabatic and relativistic approaches support our current intuitive picture of molecular processes at low orders, the higher-order corrections, necessary for a quantitative agreement with the most precise experiments, become increasingly complicated (formally and numerically) and are always limited to some finite order. For this reason, I will speak about complementary perturbative [[J. Chem. Phys. 151, 014113 \(2019\)](#); [Phys. Rev. Lett. 125, 213001 \(2020\)](#)] and variational [[Mol. Phys. 117, 590 \(2019\)](#); [J. Chem. Phys. 154, 224110 \(2021\)](#)] approaches to the non-adiabatic and relativistic problems of molecular quantum theory. I will sketch theoretical, algorithmic, and computational challenges that were recently met and that are still open for small atomic and molecular systems in relation with (ultra-)high-resolution spectroscopy experiments.