

When compared to catchy (and genuinely fascinating) bleeding-edge physical problems, such as the string theory, quantum gravity or quantum information, the fight for yet another significant number in the dissociation energy of the molecular hydrogen may appear as some kind of bookkeeping. Or „art for art’s sake” even, practised by a narrow group of enthusiasts. However, under this pretence lays an intriguing class of problems waiting to be solved.

Modern spectroscopy allows for very precise measurement of the properties of atoms and molecules, like the energies of transitions between their electronic states or the energy needed to break a chemical bond. It gives quite a good insight into the structure of the matter that our world consists of. Trying to recreate these results with means of theory, we can verify how well we understand the laws of physics. Getting the result that’s in agreement with the experiment up to many significant digits is very satisfying indeed and increases awe of the elegance of the Nature. If a discrepancy appears, which doesn’t vanish with the improvement of numerical techniques and their precision, all the better – it means that there’s something new out there to investigate and understand. It’s an enthralling puzzle, which also has an important practical application. If we compare the results of precise measurement with theoretical values, we’re able to determine certain physical constants, such as the R_∞ Rydberg constant or the proton charge radius. The latter has recently earned some interest, due to a theory-experiment discrepancy, which hasn’t been definitely explained yet. Moreover, it sometimes happens that it’s the very accurate theoretical result which allows to find the experimental error, like in the famous case of Kołos and Wolniewicz, who obtained the energy of dissociation of H_2 that was more accurate than the spectroscopic measurement of Herzberg, a future nobelist.

To match the spectroscopic measurements on the side of theory, it’s required not only to employ the ‘standard’ (nonrelativistic) quantum mechanics, but also calculate the relativistic and quantum-electrodynamical (QED, which is considered to be the most profoundly tested physical theory) effects. Furthermore, it’s also obligatory to consider that despite the commonly assumed approximations (adiabatic and Born-Oppenheimer), the electrons in atoms and molecules don’t just move around the static nuclei, but in fact all particles move. It’s a bit like the approximation that the Earth revolves around the static Sun – sufficient for everyday use, but not entirely true. The number of all these corrections starts to be a bit overwhelming, so it’s necessary to use some systematic way to consider them. In this case ‘some’ means so-called ‘nonrelativistic quantum electrodynamics’ (NRQED) – which takes care of the relativistic and QED corrections, and ‘nonadiabatic perturbation theory’ (NAPT) – which enables us to describe the nonadiabatic effects properly. Together they span a 2D array of corrections that can be calculated. Many of them are known already with a decent accuracy. However, there still is a theory-experiment discrepancy – at the 8th significant digit. It can look quite unimportant, but interestingly the last precise calculations *increased* the difference instead of making it smaller. The main suspect here is the so-called leading relativistic nonadiabatic correction, which is the first ‘mixed’ (NRQED-NAPT) term in our array.

Its accurate evaluation is the goal of this project. It’ll not only enable us to check if the theory works fine, but, as mentioned earlier, it’ll unlock the way of further improvements in determination of physical constants. Maybe it’s less important for the general public, but it’s definitely equally crucial for us that the task requires the use and testing of interesting theoretical methods and tricks, which are the things that can be considered fun by a theoretical physicist or chemist!