QED effects in molecules : vacuum polarization in a Gaussian basis set

Ryan Benazzouk^{1, †}, Maen Salman², Trond Saue¹

¹Laboratoire de Chimie et Physique Quantique, CNRS, Université Toulouse III Paul Sabatier, Toulouse, F-31062 France ²Laboratoire Kastler Brossel, Sorbonne Université, CNRS, ENS-Université PSL, Collège de France, Paris, F-75005, France

†corresponding author's email: ryan.benazzouk@irsamc.ups-tlse.fr

Recent developments have raised a new spark of interest for Quantum Electrodynamics (QED), from high-precision experiments to search for physics beyond the Standard Model. For instance, high-precision QED calculations for molecules could be of key importance in the search for new physics. As very intense electromagnetic fields are generated by heavy atoms inside molecules, the sensitivity of experiments probing for violations of the Standard Model predictions is greatly improved [1].

However, it is unclear to what extent QED can be relevant to describe molecular properties. It is now well known that relativistic effects play a prominent role in predicting properties of molecular systems containing heavy elements, and they can be computed to such high precision that correlation effects become the main source of error. But as correlation methods progress, the point approaches at which those effects compare with the magnitude of QED corrections [2]. One can then wonder if QED is needed for more precision in quantum chemistry, and to understand molecular structure or properties of the electronic density in the vicinity of heavy nuclei.

Before investigating this matter, some caveats need to be addressed. One has to do with the perturbative expansion of the S-matrix. This approach to QED has worked marvelously to clarify the reasons for divergences appearing in radiative loop-corrections, and their subsequent treatment. However, in the case of bound-state QED, the S-matrix should also be expanded in powers of the coupling constant to the nuclear potential $Z\alpha$, and this can become problematic when the coupling parameter approaches 1.

We should also mention that the S-matrix formalism deals rather poorly with electron correlation, as it requires very high orders of perturbation theory. Therefore, this approach may simply be too cumbersome for quantum chemistry, and one could aspire to a formulation of the theory that fits with the mathematical apparatus of molecular physics. Thankfully, such a program has already been proposed by Chaix & Iracane [3], and extensively studied by mathematicians [4, 5]: the Bogoliubov-Dirac-Fock model. The merit of this approach is that it yields a mean-field effective extension to the Dirac Hamiltonian that includes QED effects, reviving Dirac's interpretation of a negative energy sea, in a formalism akin to quantum chemistry. The QED effects, self-energy and vacuum polarization, arise respectively as an exchange and an electric potential generated by charge distribution in the polarized vacuum.

The goal of the HAMP-vQED project is therefore to provide a method for calculating QED effects on the electronic structure of molecules in the framework of quantum chemistry. Effective potentials already exist to target valence electrons, but we suspect that they might not be as reliable for core orbitals that undergo very intense electric fields. To do so, we then aim to compute vacuum polarization density and self-energy corrections using Gaussian-type basis sets [6, 7].

In this contribution, I will present my work on vacuum polarization in a finite basis, more specifically our results on energy shift calculations and our method for regularization. I will show how various aspects of vacuum polarization around a nucleus can be computed accurately in a finite Gaussian basis set.

References

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