

# Thesis (theoretical chemistry): Effect of quantum electrodynamics on molecular properties

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Although the special theory of relativity seems deeply entrenched in the domain of physics and perhaps far from everyday experience, it has during the past thirty years been realized that relativistic effects have a profound impact on chemistry [1,2]. Without relativity gold would have the same color as silver [3], mercury would not be liquid at room temperature [4] and your car would not start [5]. A relativistic description of electrons is obtained by switching from the Schrödinger to the Dirac equation. A challenging aspect of the Dirac equation is that in addition to solutions of positive energy, equivalent to non-relativistic theory, it also features solutions of negative energy. Although the gap between these two branches of solutions is considerable, on the order of  $2m_e c^2$ , quantum leaps from the positive-energy to the negative-energy branch are possible and would make matter unstable. Quite early it was for instance pointed out that the relativistic hydrogen atom would have a lifetime of only one nanosecond. Dirac found a solution to this problem by postulating that all the negative-energy states were occupied by electrons, which, due to the fermionic nature of electrons, would block any downward transition of bound electrons. On the other hand, since the negative-energy electrons are never observed directly by experiment, if sufficient energy ( $\sim 2m_e c^2$ ) were to be pumped into the vacuum, one would see not only the appearance of an excited positive-energy electron, but also the hole of positive charge it leaves behind, corresponding to the anti-particle of the electron, the positron.

In present-day relativistic molecular calculations, the negative-energy solutions are projected out and thus ignored. A proper description of electrons and positrons requires further refinement in the form of quantum electrodynamics (QED), where the negative-energy solutions take on physical reality. In fact, with the introduction of QED the vacuum becomes a polarisable medium, with the incessant creation of virtual electron-positron pairs. An experimental manifestation of such QED effects is the Lamb shift, which is a tiny splitting of about 4 meV between the  $^2S_{1/2}$  and  $^2P_{1/2}$  states of the hydrogen atom, although predicted to be degenerate by Dirac theory. For hydrogen-like uranium this splitting has grown to 469 eV. It is therefore legitimate to ask if QED effects could affect the chemistry of the heavy elements.

A partial answer has been given by Pekka Pyykkö and co-workers [2, 6, 7] who has investigated QED effects (dominated by vacuum polarization and the self-energy of the electron) on the valence properties of heavy atoms. They find for instance that whereas 23 % of the ionization potential (IP=9.23 eV) of gold is due to relativity, QED reduces the relativistic effect by about 1 %. This seems to suggest that QED effects need not be included in quantum chemical calculations involving heavy elements unless very high accuracy is desired. However, QED effects are expected to be much more significant for molecular properties probing the electron density in the core region. Indeed, for the 1s binding energy (34566 eV) of the xenon atom, QED effects (-41 eV) are an order of magnitude more important than electron correlation (3 eV) [8]. Furthermore, Pyykkö and Zhao have suggested that QED effects on NMR parameters may be as important as solvation effects [9]. More recently, Gimenez and co-workers estimated QED effects on NMR shielding constants for He- and Be-like atoms by scaling of hyperfine integrals based on orbital energy changes when QED effects were added perturbatively in atomic calculations [10]. These are, however, rather crude estimates and require validation, which is the main objective of the present proposal. More rigorous calculations have been reported by Yerokhin *et al.* [11], but these are limited to hydrogenlike ions, with no straightforward extension to many-electron molecular systems. QED effects may also be amplified by extreme conditions such as strong magnetic fields, intense laser beams or high pressure. The latter situation is particularly interesting for the present project. Simulations of molecules under high pressure or under confinement (for instance, inside a nanostructure) is often carried out with the introduction of a confinement potential, typically a 3D harmonic potential (e.g. [12]). It is, however, known that the Dirac equation for a 3D harmonic oscillator has no bound solutions [13]. The extension of such calculations into the relativistic regime will therefore require proper handling of the negative-energy solutions, an issue to be addressed by the present project.

QED is a marvel of modern science, allowing predictions of accuracy beyond that of experiment. Yet QED in its present perturbative formulation only allows precise calculations on few-electron atomic systems [14]. There is therefore

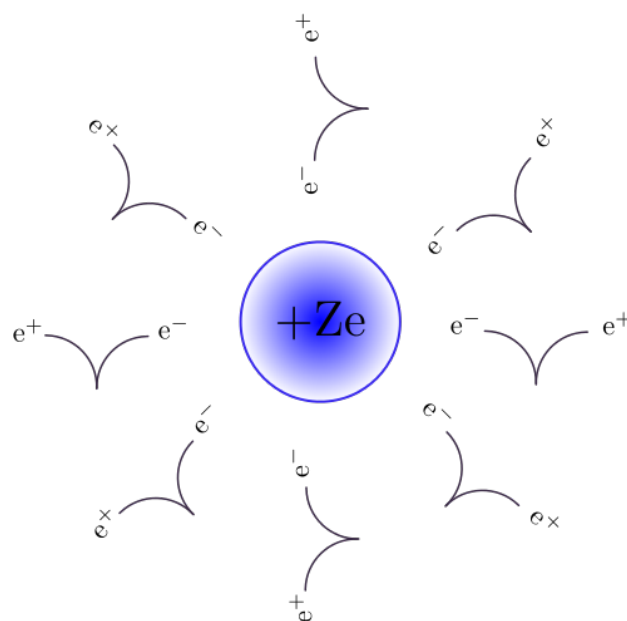


Figure 1: A simple model of vacuum polarization.

considerable interest in the domain of relativistic quantum chemistry to develop methods for the incorporation of QED effects in molecular calculations of chemical relevance. Based on previous work by Chaix and Iracane in 1989 [15], the present principal investigator in 2003 [16] formulated Hartree-Fock theory including vacuum polarization and subsequently programmed it in the relativistic molecular code DIRAC [17], of which he is one of the main authors. Recently this idea has been picked up by other authors [18–22].

The present project is based on a very original interdisciplinary collaboration between the relativistic quantum chemistry group in Toulouse and a group of mathematicians in Paris. We will also join forces with Peter Schwerdtfeger (Massey University, New Zealand) and Ephraim Eliav (Tel Aviv), both experts on relativistic atomic and molecular calculations as well as QED [14, 18].

*The main objective of the present proposal is to investigate the importance of QED effects in chemistry.*

We plan to proceed by two major steps:

1. A simple approach for the inclusion of QED effects is based on the use of effective potentials [9, 14, 23, 24]. We plan to implement the **effective QED potentials** of Shabaev and co-workers [24]. They have been developed for atomic calculations, but we will adapt them for molecular ones using atomic projectors. With these corrections at hand we will next investigate **QED effects on molecular properties of chemical relevance**:
  - (a) X-ray absorption and Mössbauer spectroscopy of heavy elements.
  - (b) NMR parameters (shielding and indirect spin-spin coupling)
  - (c) molecules in extreme conditions (confinement, high pressure, intense electromagnetic fields) believed to accentuate QED effects
2. A more ambitious and therefore also risk-prone approach is to explicitly include the negative-energy solutions in a QED extension of variational quantum chemical methods such as Hartree-Fock or Kohn-Sham. We plan to develop **fully variational QED for molecular calculations**. This challenging step calls for close collaboration between theoretical chemistry and mathematics.

***The role of the PhD-student is to pilot the implementation and application of necessary theory in the DIRAC code. The candidate should be trained in quantum chemical calculations, preferably on molecular properties, and have some programming experience. Interested candidates are invited to send a letter of motivation and their CV.***

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