

Valence-shell QED effects in heavy-element compounds

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Valence-shell quantum-electrodynamical terms (QED), whose two leading terms, of opposite sign, are the self-energy (SE) and vacuum polarization (VP), are of interest for three different reasons: 1) To the extent that they are small, this smallness justifies the current Dirac-level models, 2) Actually the accuracy of present quantum chemistry, in the domain from water to the superheavies, is now approaching the level where not only relativistic, but QED effects will soon be seen in a head-on comparison between *ab initio* theory and experiments, 3) These terms may have been 'the last train from physics to chemistry' at the level of fundamental Hamiltonians.

A large number of careful studies of these effects exist for few-electron atoms. A few examples will be shown. The fundamental way of treating these terms is to first create a complete basis of one-particle states and to then evaluate the relevant Feynman diagrams. This can also be done for the SE of valence electrons in neutral, or nearly neutral atoms, to the extent that an effective one-electron potential is available [1]. For the lowest-order VP term, a local potential by Uehling and Serber in 1935 is available. Various approximate methods have also been tried [2].

To give an idea of the orders-of-magnitude, for heavy elements ($Z > 50$), the QED effects cancel about 1% of the Dirac-level relativistic effects [1], for the energy shifts of *ns* valence electrons. For the ionization potential of the gold atom this means about -0.3% of the total value. Here it should be mentioned that the very first estimates for Cs and Fr were published by Dzuba et al. [3] already in 1983.

The VP part is to lowest order a local potential, a property of space, same for all elements. Would it be possible to find an effective potential, simulating the SE terms? For energy-only this can be done. Probably any 'broad δ -function' at the nucleus with a right norm will do the job. An example is the work by Fricke in 1971 [4]. For several simultaneous properties such an effective potential has not been attempted, to our knowledge, before Pyykkö and Zhao [5], who fitted the SE effects on the energy and the magnetic-dipole hyperfine integrals of 2s states. Note that both the relativistic and the QED effects are smaller for the 1s states than for the higher states. The V_{SE} used was a simple Gaussian, $B \exp(-\beta r^2)$. Finally, a quadratic fit of the height B and the width parameter β to the nuclear charge was made for the fitting range $Z=29 - 83$. The final results were tested over this range and above it, up to the superheavy alkali metal E119. Recent, more fundamental results are available for the hyperfine effects of the alkali metals Li-Fr by Sapirstein and Cheng [6]. For properties close to a threshold, the percental QED effects can become very large. An example is the electron affinity of eka-radon, E118, where a decrease of -9% is obtained [7]. The final calculated EA is -0.064(2) eV.

References

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