Using effective QED potentials in molecular calculations

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Improvements in both computational power and methodology nowadays allow highly accurate electronic structure calculations including both relativistic and electron correlation effects. A next challenge for increased accuracy is the inclusion of the effects of quantum electrodynamics (QED), notably the electron self-energy and vacuum polarization, which in principle means going beyond the no-pair approximation [1,2].

Calculations within the rigorous QED framework are reported for few-electron systems, but this approach cannot be extended to many-electron systems because of the high computational cost. A more practical, but approximate approach is the introduction of effective potentials to incorporate QED effects. In the atomic case, some codes for the calculation with effective potentials are reported [3,4], and their application show that this approach leads to excellent agreement with experiment [5].

Meanwhile, in the case of molecules, the methods to incorporate QED effect are limited to pseudopotentials (e.g. [6,7]) and model potentials [8], which are obtained by parameter fitting. Although the former approach can describe the electronic structure of the valence orbitals well, they cannot calculate core-level properties and the disagreement with more elaborate potentials is non-negligible [5].

In this work, we report the first implementation of effective QED potentials in a program for all-electron 4-component relativistic calculations, DIRAC [9]. We have implemented three kinds of potentials: the Uehling potential [10] for vacuum polarization, Pekka and Zhao's model potential [8], and Flambaum and Ginges's effective potential for self-energy effects [11]. The one-electron integrals for these potentials are evaluated numerically, and are available for all electronic structure methods available in DIRAC. In our presentation, we show some results of sample calculations.

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