Developing a Deeper Understanding of the Nature of the Electron in Atomic and Molecular Systems: A Survey of Relativistic Quantum Chemistry

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In 1929 Dirac published an equation which for the first time properly unified the natural laws of quantum mechanics and special relativity. The Dirac equation offers a more precise extension of quantum mechanics which is better suited to describe features such as the inherent spin of the electron and the behavior of electrons in heavy atoms, where electrons can approach speeds that are a significant fraction of the speed of light. The inclusion of relativistic phenomena such as spin-orbit coupling and orbital contraction is necessary for the understanding of many chemical systems, and when naively overlooked in non-relativistic electronic structure calculations can often lead to results which are qualitatively misleading. By re-examining elementary quantum systems under the Dirac equation, a deeper understanding of the nature of the electronic structure of atomic and molecular systems will be pursued.

In the extension of the Dirac equation to a self-consistent field theory, the question of how to account for electron correlation has many possible answers. Relativistic electronic structure methods, which make no approximation to the many-body four-component wave function, often have astronomical costs, especially for the heavy-element chemistry for which they are so crucial. Among the many available correlation methods which build upon the relativistic Dirac-Fock self consistent field approach, the relativistic coupled-cluster method is chosen to discuss the performance and cost of four-component methodology versus the non-relativistic analog. By introducing approximations, the two-component approaches alleviate some of the expense associated with the four-component schemes. The most popular of these two-component methods, the Douglas-Kroll-Hess approximation, will be discussed in more detail.

References
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