

IDEAS OF RELATIVISTIC QUANTUM CHEMISTRY

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Fundamental breakthroughs have recently been achieved in relativistic quantum chemistry for both electronic structure and magnetic properties:

(1) Electronic structure

For any quantum mechanical calculation one has to first choose an electronic Hamiltonian, the best of which must be something between the Dirac and Schrödinger equations. Here we propose an exact two-component (X2C) equation[1-6], which is conceptually simple, numerically accurate, and computationally efficient. In addition, it serves a seamless bridge between the Dirac and Schrödinger equations, in the sense that it allows for relativistic treatment of the heavy atoms and non-relativistic treatment of the light atoms in the molecule in a natural manner.

(2) Magnetic properties

Four-component relativistic theory of magnetic properties such as NMR shielding tensor is formally very simple: It consists only of a single term, the paramagnetism. Yet, it is plagued by two fundamental issues. Conceptually, the diamagnetism known from non-relativistic theory is “missing”. Computationally, such a standard formulation is very demanding on basis functions of high angular momenta. Herewith we propose several strictly equivalent approaches [7-9] based on the generic ansatz of orbital decomposition [10, 11]. Not only does the diamagnetism arise naturally, but also is the computation simplified greatly. The X2C counterparts have also been formulated in a most general way [12].

The X2C Hamiltonian can be combined with know-how correlation methods so as to generate a new generation of relativistic many-body theories for the whole Periodic Table of elements.

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