Infinite-Order Douglas–Kroll–Hess Theory

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Exact decoupling of positive and negative energy states of the Dirac Hamiltonian, which has previously been achieved by Barysz and Sadlej with unitary transformation techniques in a purely numerical scheme [1], is discussed in the framework of the Douglas–Kroll–Hess method [2]. A very important aspect in this procedure is that such a two-component method must never make any reference to a small component; i.e., no intermediate use of the small component's basis for the construction of operators in matrix representation is allowed.

It is discussed that all block-diagonalization protocols for the Dirac Hamiltonian have *necessarily* to start with an initial free-particle Foldy–Wouthuysen step [2]. Any higher-order FW transformation is in principle not defined (i.e., an expansion of the Hamiltonian in $1/c$ is not allowed).

The DKH protocol [3], employing an expansion of the Dirac Hamiltonian in even terms of ascending order in the external potential, yields the only well-defined and regular expressions for any order if an *analytic* unitary transformation scheme for the Dirac Hamiltonian is sought for [2]. In recent years, the DKH Hamiltonians up to sixth order have attracked much attention [4].

Its exact infinite-order version DKH∞ can in principle not be realized by a straightforward *numerical* iterative extension of the DKH procedure to arbitrary order within one-component electronic structure programs [2]. It is important to note that the order in the external potential necessary for exact decoupling (i.e., decoupling up to machine precision) is determined prior to any quantum chemical calculation [4]. Once this maximum order has been determined, the spectrum of the positive-energy part of the decoupled Hamiltonian, cannot be distinguished from the corresponding part of the spectrum of the Dirac operator [5]. In this sense an infinite-order DKH formalism is established.

A sophisticated ansatz based on an analytic evaluation of the DKH operators up to *any* pre-defined order via a suitable symbolic parser routine has to be employed instead [5]. Its algorithmic principles and its efficient scalar-relativistic implementation are shortly discussed.

References:

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