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無限次 Foldy-Wouthuysen 変換による化学シフトの相対論的効果の計算

(北見工大) ○今西佐織, 工藤慶一, 福井洋之

Fully relativistic treatments based on the four-component spinor form of the one-electron wave functions, are still very costly, primarily due to the cost for a proper description of the small two-component spinor. In most relativistic quantum chemistry problems, however, explicit consideration of the negative energy states or the electron-positron pair creation processes is unnecessary. For example, the information included in the four-component Dirac equation is excessive for the majority of problems encountered in relativistic quantum chemistry. Thus, the investigation and development of more appropriate two-component methods is particularly attractive. Many methods have been proposed to reduce the four-component Dirac formalism to computationally much simpler two-component schemes. Two groups of approximate two-component methods have been successful thus far; methods based on the Douglas-Kroll-Hess (DKH) approach [1],[2], and those based on the regular Hamiltonian approximation (RA) [3],[4].

A powerful approach to decoupling positive energy states (electronic states) and negative energy states (positronic states) is the Foldy-Wauthuysen (FW) unitary transformation[5]. However, except for a free particle, the exact decoupled Hamiltonian H^{FW} is not known in closed form. Unfortunately, if H^{FW} is replaced by a truncated expansion in c^{-1} (reciprocal of the speed of light), the electronic Hamiltonian h_+ is not bounded from below and is variationally unstable [6]. In the 50-year history of research in this area, exact, closed-form expressions of the h_+ Hamiltonian have not appeared. Recently however, a breakthrough in this field was made by Barysz and Sadlej (BS) [7], who showed that a numerical but exact Hamiltonian matrix of h_+ can be obtained by matrix multiplication.

The present authors have already presented relativistic calculations of nuclear magnetic shieldings in hydrogen halides based on the DKH method [8]-[11] and zeroth-order regular approximation (ZORA) [11]. However, the results of these two approaches differ considerably, rendering it still necessary to establish an accurate and reliable scheme for evaluating nuclear magnetic shielding tensors. In the present work, the method of Barysz and Sadlej, the BS method, is extended to include a vector potential, and is applied to computation of the nuclear magnetic shielding tensors of hydrogen halides.

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