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Calculation of nuclear magnetic shielding constants using variation-perturbation method with moderate size basis sets

V.B. Mushkin, R.M. Aminova*

Department of Physics, Kazan State University, 18 Kremevskaya Str., Kazan 420008, Tatarstan, Russian Federation

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Abstract

Within a framework of variation-perturbation formalism of Karplus–Kolker, an algorithm and a program for the nuclear magnetic shielding calculations with ground-state wave functions were developed. The calculations of nuclear magnetic shielding σ in some diatomic molecules and also in methane, water and CH_3F molecules with 6-311G ab initio wave functions were carried out. The results were compared with the experimental data and the results obtained by other theoretical methods. This method can be considered as an alternative approach for the calculations of the magnetic anisotropic effects on chemical shifts and can be used for predicting the tendencies in magnetic shielding alteration due to the different fragments in a big molecular systems. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nuclear magnetic shielding constants; Variation-perturbation method; Diatomic molecules; Methane; CH_3F

1. Introduction

Spectroscopy of nuclear magnetic resonance (NMR) is one of the most widely used methods for research molecular structure and dynamics. Though the experimental methods of NMR spectroscopy have a great progress, the theoretical interpretation of parameters experimentally detected — chemical shifts — is still an urgent problem. A lot of reviews were dedicated to various aspects of chemical shift theory, starting with reviews edited by Raynes, Harris, Webb (e.g. Ref. [1], and also Refs. [2,3]).

The history of nuclear magnetic shielding theory evolution is very saturated and includes the whole set of quantum mechanics methods beginning with the traditional perturbation theory (see Ref. [4]), and

including such moderate methods as the Second-Order Polarization Propagator (SOPPA) method [5,6] (see also Ref. [1]) and density functional theory (DFT) [7], taking into account electron correlation effects.

Along with the perturbation theory the variation methods for the calculations of second-order magnetic properties were developed (see Refs. [4,8,9]). Their advantage is that they do not require the knowledge of continuous energy spectra of the molecule, which is very important, and allows to calculate the chemical shifts by using the molecular wave function of a ground state [10,11]. In the works of Karplus and Kolker [8,9], the formalism of variation-perturbation theory was developed. It was shown that this approach predicts successfully the chemical shifts of diatomic molecules both for light and for heavy nuclei. This method was expanded further in the works of Sadley [12], where the coupled variant of this method was

* Corresponding author. Tel.: +7-8432-387614.

E-mail address: raminova@rambler.ru (R.M. Aminova).