JOURNAL OF MAGNETIC RESONANCE 33, 497–503 (1979)

Calculation of Nuclear Magnetic Shielding Constants by the Method of Gauge-Invariant Atomic Orbitals Using Gaussian Functions

R. M. AMINOVA, H. I. ZOROATSKAYA, AND YU. YU. SAMITOV

Kazan State University, Department of Chemistry, Kazan 420 008, U.S.S.R.

Received February 1, 1978; revised June 22, 1978

It has been shown that the using of the gauge-invariant atomic orbitals together with Gaussian expansion of orbitals allows one to obtain satisfactory results for the proton magnetic shielding constants without an average excitation energy approach, the wave functions being obtained by any MO LCAO method. It is necessary to employ a more complicated variation function for the calculations of ^{13}C shielding constants. The proton and ^{13}C shielding constants have been calculated for a number of molecules (CH_4, C_2H_6, CH_3NH_2, CH_3OH, CH_3F). The simple functions, obtained by extended Hückel and INDO methods have been used as unperturbed solutions. Comparison with *ab initio* calculations and experimental data have been carried out.

INTRODUCTION

The wide use of NMR spectroscopy for the molecular structure investigations makes urgent the problem of chemical shift estimation, which could allow one to obtain the satisfactory results with the least effort. There are a number of theoretical methods to calculate the nuclear magnetic shielding constants in molecules. Among them the coupled perturbed Hartree–Fock formalism (*1*) is the most nearly correct, the wave functions in the presence of a uniform external magnetic field being determined by self-consistent field perturbation theory. This method for the achievement of gauge-invariant results for magnetic shielding constants, however, requires too large a basis set of atomic orbitals, close to a complete set. In the framework of this approach even the calculations of magnetic properties of diatomic molecules require considerable computational efforts.

In contrast to (*1*) the molecular orbitals in the paper (*2*) are written as linear combinations of gauge-invariant atomic orbitals (GIAO). Such functions relating to the problems of molecular diamagnetism in aromatic hydrocarbons were introduced previously by London (*3*) and have been used later in nuclear magnetic shielding calculations (*4–6*). It is necessary to emphasize that the solution of Hartree–Fock equations by taking into account a magnetic field requires the creation of rather complex special programs.

In paper (*7*) we have reported a simple method which allows calculation of the nuclear magnetic shielding without an average excitation energy approach, the wave functions being obtained by any MO LCAO method: the simple MO LCAO method

0022-2364/79/030497–07$02.00/0

Printed in Great Britain