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CALCULATIONS OF MAGNETIC SUSCEPTIBILITY OF SOME MOLECULES BY THE VARIATIONAL METHOD USING AB INITIO WAVE FUNCTIONS

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ABSTRACT

Calculations of magnetic susceptibility were carried out for H_2O, CH_4, NH_3, PH_3 and H_2S using the variational method with non-empiric wave functions. It was established that the results are weakly sensitive to the basis set. It was shown that the results are comparable with the more precise results obtained by the coupled Hartree–Fock (CHF) method and agree well with experimental data. It should be noted that requirements to gauge invariance are considerably lower than in the CHF method.

INTRODUCTION

In the last few years the interest in calculation of so-called second-order molecular magnetic properties has grown. It is well established that the coupled Hartree–Fock (CHF) method [1] can yield the values of magnetic parameters within experimental accuracy [2–5]. However, its practical use seems to be limited by the requirement of a sufficiently large extended basis set. Applications of the CHF theory with use of gauge-invariant atomic orbitals (GIAO) [6,7] and the theory in terms of localized MOs and individual gauge origins for the different MOs [8,9] has diminished the requirements of basis set size. Nevertheless, it is improbable that these methods will be convenient for calculations on large molecules. Meanwhile the search for different, more accurate, semi-empirical methods for calculating magnetic properties and different fragmentary approaches applicable to large molecules is continuing. We believe that variational methods, which are known to be considerably less sensitive to the accuracy of the wave function of the unperturbed molecule (or fragment) [10,11], can be useful.

The purpose of this work is to study the applicability of the variational method for molecular magnetic susceptibility calculations, using ab initio wave functions in a rather simple basis set as the ground state wave functions. In order to avoid computational difficulties of the CHF method some simplified, so-

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