Integrals of Nuclear Shielding Tensor and Coupling Parameters over Exponential Type Functions

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Abstract The present communication concerns the analytical and numerical treatment of nuclear magnetic resonance (NMR) parameters, for instance the shielding tensor and coupling constants. These NMR parameters present severe difficulties, due to the presence of complicated operators involving $1/r^n$ (with $n = 3, 5, 6, \ldots$) in their expressions. These new operators give arise to extremely difficult integrals, especially when using exponential type of functions (ETFs) as a basis set of atomic orbitals. Magnetic properties are particularly sensitive to the quality of the basis sets due to many contributing physical phenomena arising from both the vicinity of the nucleus and from the valence region. This is why, it is highly desirable to use ETFs as a basis set of atomic orbitals, as they have a much improved form near to, and far away from, nuclei. Calculations involving a magnetic field should preserve gauge invariance. This is conveniently accomplished by using a gauge including atomic orbitals (GIAO).

The main difficulty in the computation of the shielding tensor arises from the presence of $1/r^3$ in the operators involved in their expressions, where $\vec{r}$ stands for the vector separating two particles. It is shown that these integrals can be expressed as a finite linear combination of integrals involving the operators $Y_1^j(\theta_{\vec{r}}, \varphi_{\vec{r}})/r^2$ with $j = -1, 0, 1$. By introducing the Fourier representation of the new operators, analytic expressions were derived for these integrals and they involve highly oscillatory semi-infinite integrals.

For the numerical treatment of the obtained analytic expressions, we used extrapolation methods and nonlinear transformations combined with quadrature rules and it is now shown that our algorithms are highly efficient and they will definitely lead to a software package for the computation of NMR parameters for molecules.

Keywords: Nuclear magnetic parameters, shielding tensor, molecular integrals, exponential type functions, Fourier transform, extrapolation methods, nonlinear transformations.