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Referee report on the PhD Dissertation "Relativistic Calculations of Nuclear Magnetic Resonance Spectroscopy Parameters", submitted by Ms. Małgorzata Olejniczak

The research presented in the PhD Dissertation submitted by Ms. Małgorzata Olejniczak concerns methodological developments and innovative applications in the field of the relativistic theory of the nuclear magnetic resonance (NMR) parameters. In view of the great experimental relevance of these parameters (shielding tensors and spin-spin coupling constants) their theory is one of the most important and most actively developed research areas in quantum chemistry. It is also most intellectually challenging. This challenge results from the need to use a relativistic description of the electronic motion in the proximity of nuclei (where electron velocities are very large), from the complicated magnetic field dependence of approximate relativistic wave functions, necessary to achieve the gauge-origin independence of the results, and finally from the sheer complexity of the structure of many-electron relativistic wave function and, consequently, the basis sets one has to use in the calculations. Despite these three difficulties the progress achieved in the last decade is very impressive. In her Dissertation Ms. Olejniczak made her own contribution to this progress.

Her most important achievement, presented in the Dissertation, is the development, computational implementation and pilot applications of a new relativistic method of calculating the NMR shielding constants. She used the four-component spin-density functional theory (including non-collinear spin magnetization) to account for the relativity and for the electronic correlation, the London atomic orbitals (LAO's) to achieve the gauge-origin independence of the results, and her own ingenuous procedure to construct the basis for small components of the wave function in the presence of the magnetic field (to achieve the so-called magnetic balance). Her implementation and employed approximations have been carefully validated by calculations for model molecules with varying magnitude of nuclear charge. The computer code developed by her is included in the freely distributed DIRAC code and is ready for the production runs. On can expect that its availability will increase the use of the relativistic theory of NMR shielding tensors and, therefore, will improve the reliability of the predictions made by the theory of NMR shielding.

The Dissertation of Ms. Olejniczak consists of 57-page long text written by her (in good English) presenting the context and motivation of her research, the basic theoretical concepts used, a concise description of the implementation details of her method and, finally, the discussion of the results of the performed applications. This text is followed by the impressive, 28-page long list of cited literature (332 references with corresponding URL addresses). This list will certainly be very helpful to students/readers interested in a more thorough study of the subject. The next part of the Dissertation are reprints of four journal publications, coauthored by Ms. Olejniczak, containing results of her (and other authors) work. Each of these papers (appearing in *J. Chem. Phys.*, *J. Phys. Chem.* A, *Phys. Chem. Chem. Phys.*, and in *Comput. Theoret. Chem.*) is preceded by a brief statement describing the contribution made to the published work by Ms. Olejniczak. The last part of the Dissertation, entitled "Notes 1", is a short, 7-page long text, presenting mathematical details of the connection-free formulation of the linear response theory used in the calculation of the NMR shielding tensor. The Dissertation contains also the information that Ms. Olejniczak co-authored two publications that are not included in it and are not related to its subject. Both publications contain an application work - one on the nonlinear electric susceptibilities of urea crystal and the other on the spin-spin coupling constants transmitted through a dihydrogen bond.

In my opinion this form and structure of the Dissertation is satisfactory, in fact exemplary. In writing her own text Ms. Olejniczak has shown her competence in the field of relativistic theory of NMR shielding and a good understanding of the theoretical and computational aspects of the research performed by her. She also demonstrated a considerable talent in scientific writing. By inspecting the reprints included in the Dissertation the reader can see the full picture of the research projects in which Ms. Olejniczak was involved, including the contribution of co-authors. Her contribution to the reprinted papers is always clear from the description of her research that she presented in the main text and from the statements preceding each included reprint.

I view the implementation, code and test calculations presented in the 2012 *J. Chem. Phys.* paper (co-authored by Radovan Bast, and her thesis advisers Professor Trond Saue and Professor Magdalena Pecul) as the main achievement of this dissertation. In this context I would particularly emphasize the excellent efficiency of the simple (inexpensive) scheme of achieving the magnetic balance (referred to as simple magnetic balance sMB) proposed in the *J. Chem. Phys.* paper. As demonstrated in Table III of this paper, when conventional basis sets are used the sMB scheme gives results practically identical with the results obtained with the expensive, unrestricted kinetic balance (UKB) and much better than one can obtain with the standard (field independent) restricted kinetic balance (RKB).

The remaining three papers included in the Dissertation also contain interesting and important results. I particularly like the 2011 *J. Phys. Chem.* A paper presenting a very nice theoretical-experimental collaboration. Ms. Olejniczak contribution to

this paper was the calculation of the relativistic correction to the shielding constant of the ^{31}P nucleus in the PH_3 molecule. She used the method developed by her. When combined with the results of very accurate nonrelativistic calculation by Professor Jaszuński and with the gas-phase measurements performed in prof. Jackowski's group in Warsaw, this correction enables a new, more accurate determination of the magnetic dipole moment of the ^{31}P nucleus.

The contribution Ms. Olejniczak made to the paper published in *Comput. Theoret. Chem.* also involves an application of the method developed by her. She provided the four-component calculations of the relativistic corrections to the shielding constants in diatomics containing the N, P, and As atoms. Her results showed that for the As nucleus these corrections cannot be determined reliably at the Hartree-Fock level, i.e., that the cross, relativistic-correlation terms are important. This paper contains also an interesting discussion of alternatives to the nonrelativistic Flyger formula, relating the electronic contribution to the spin-rotation constant with the paramagnetic part of the shielding tensor. It is not clear, however, what was the involvement of Ms. Olejniczak in this part of the published work.

The last paper included in the Dissertation, published in *Phys. Chem. Chem. Phys.*, presents the implementation, made by Ms. Olejniczak, of the London atomic orbitals and simple magnetic balance in four-component calculations of magnetic induced current density in a molecule. Although the current density cannot be measured, this software can be used for the visualization of the magnetic field effects in heavy molecules.

I do not have essential critical comments on this Dissertation. I noticed, however, several, mostly minor errors or problems in the main text written by Ms. Olejniczak. One more general remark is that not all used acronyms are explained. One example is CGO (common gauge origin). This acronym is explained only in the included *J. Chem. Phys.* reprint. Clearly, a separate list of used acronyms would have been very useful. Another problem I see is the not consistent treatment of units. The Author writes that the "SI atomic units are used", which is a nonsense (SI and atomic units are completely different). I think, it would have been better to use the SI units consistently. For instance, if $\vec{I}_K$ is really a nuclear angular momentum operator, then the Planck constant $\hbar$ in Eq. (1.1) is superfluous (with the conventional definition of the gyromagnetic ratio $\gamma_K = g\mu_N/\hbar$). I also found a few places with simple errors. For instance, in the Breit Hamiltonian, Eq. (2.37), the factor of 1/2 is missing in the second term. In the middle of page *vii* the Author incorrectly states (in Polish) that the kinetic balance depends on the angular momentum operator (operator momentu pędu). The first sentence in Sec. 2.2 is not correct. The rotation (curl) of the scalar χ is not defined. One simply can add to $\vec{A}$ a gradient of any scalar χ, cf. Eq. (2.13). The statement on the electron density at the very top of page 34 is trivial. The converse statement is nontrivial and forms the basis for the DFT theory. These are minor points and do not diminish my high opinion about this dissertation.

It should be pointed out that the theory of the NMR parameters is a very active research area and Ms. Olejniczak was not the only person working on the relativistic DFT theory with London orbitals. She had to face a strong competition from excellent research groups. In fact, the first implementation of the four-component relativistic DFT theory with London orbitals, in many aspects similar to the one presented in her thesis, has been developed in the group of Olga Malkina and Vladimir Malkin in Bratislava. Another approach has been independently developed by Wenjian Liu's group in Beijing. This competition is the sign of the relevance of her work and in no way diminishes her achievement.

Ms. Olejniczak begins her Dissertation with the citation from Wisława Szymborska's 1996 Nobel Lecture: "Any knowledge that doesn't lead to new questions quickly dies out." She fittingly finishes the main text with her own list of important problems remaining for future research. I share her perspective and view this list as very well chosen. This list shows that Ms. Olejniczak is now a mature researcher who can chose her own important research problem and can successfully pursue its solution.

Summarizing this report I would like to state that Ms. Olejniczak presented a very good Ph.D. Dissertation, certainly belonging to the best 20% of dissertations presented at our Department . The results of the research reported by her are highly nontrivial. The methods she developed are expected to contribute in a significant way to the set of tools available to a chemist interested in a computation and a better understanding of the NMR shielding constant. Some minor critical remarks given above do not change my very positive opinion about her work. Ms. Olejniczak has proved herself as a very competent theoretical and computational chemist, capable of solving difficult problems in the field of electronic structure theory of NMR parameters. The research she performed and reported in her dissertation is an evidence of her talent and stamina needed to succeed in science.

Conclusion: I ascertain that the Ph.D. Dissertation of Ms. Małgorzata Olejniczak complies with all the requirements imposed on doctoral dissertations, and hereby I express my consent to continue further with the doctoral procedure. Because of the difficulty of the problem she considered and the importance of the obtained results I view her dissertation as a distinguished one.

Podsumowanie: Stwierdzam, że rozprawa doktorska p. mgr Małgorzaty Olejniczak spełnia bez zastrzeżeń wszystkie wymagania stawiane pracom doktorskim. Wnoszę zatem o dopuszczenie mgr Olejniczak do publicznej obrony jej rozprawy. Ze względu na złożoność rozważanego zagadnienia naukowego i wagę uzyskanych rezultatów oraz ogólnie rzecz biorąc bardzo wysoki poziom rozprawy proponuję jej wyróżnienie.

Bogumił Jeziorski