

Dr hab. Mariusz Paweł Mitoraj
Department of Theoretical Chemistry
Jagiellonian University
30-060 Krakow, ul.: Ingardena 3
Poland
email: mitoraj@chemia.uj.edu.pl
TEL (+4812) 220-2042



JAGIELLONIAN UNIVERSITY
IN KRAKÓW

A review of the PhD thesis entitled “Developing New Quantum Chemistry Methods Based on Extended Random Phase Approximation” by Koushik Chatterjee. It has been prepared under supervision of Prof. Katarzyna Pernal.

General remarks

The PhD thesis of Koushik Chatterjee is focused on very critical, extremely challenging, issues of the modern quantum chemistry – namely, development of possibly low-cost and accurate methods (capable to capture both static and dynamic electron correlation effects) suitable for description of excited states as well as bond-breaking processes. These are extremely important issues for understanding and prediction spectroscopy, as well as modelling of chemical reactions.

The candidate has successfully developed and tested the following new methods of quantum chemistry: (1) ERPA (Extended Random Phase Approximation) and ERPA2 (containing double excitations) (2) TD-APSG (Time Dependent version of the Antisymmetrized Product of Strongly orthogonal Geminals) (3) TD-GVB (time dependent version of the Generalized Valence Bond method) (4) ERPA-GVB (the GVB-PP corrected for the intergeminal dynamic correlation). The results have been published in the five high quality papers of the topical journals in the field: *J. Chem. Phys.* 137, 204109 (2012), *J. Chem. Phys.* 140, 014101 (2014), *J. Chem. Phys.* 144, 244111 (2016), *Theor. Chem. Acc.* 134, 118 (2015), *Theor. Chem. Acc.* 135, 246 (2016), and one publication as a book chapter in the series *Highlights in Theoretical Chemistry*, 2015, Vo. 12, 219-227. Additionally, the candidate was a principal investigator in the Preludium grant (DEC-2014/13/N/ST4/03990) of the National Center in Poland (NCN), as well as participated in the POMOST grant (POMOST/2010-1/6) of Foundation for Polish Science (FNP). Mr Chatterjee has presented his results during international and local conferences (one poster in USA and three talks in USA, Bulgaria and Poland). These are, in my opinion, very impressive scientific achievements, which prove that, although the candidate is an early stage scientist, he is able to creative solving quantum chemical problems (related to both methods, numerical algorithms developments and their practical implementations). Such skills are especially valuable nowadays since the market becomes more and more dominated by “pure” applicative works (which are also important) – without the priceless methodological efforts, which are very often very long-term investments and often not-enough appreciated, it would be impossible to reach the current stage, where, for example, large proteins or catalytic reactions are modelled by various methods of quantum chemistry. From this respect the objectives of the thesis of Koushik Chatterjee are very timing.

Detailed comments

The PhD thesis is organized in typical sections: (1) Theoretical Background (25 pages), Results (chapters 1-6, 75 pages), Summary (2 pages) and Bibliography (175 positions). The PhD is well written in English and the graphical content has been very

carefully prepared. It is also useful for a reader, and shall be praised, that the candidate has concluded each chapter separately.

The chapter 1 presents, in an exhaustive way, the theoretical background starting from time-dependent Schrödinger equation, going through Hartree-Fock, post-Hartree-Fock methods, first and second order density matrices and the related DMFT theories and ending up with the two electrons based geminals, equation of motion by Rowe and the corresponding TDA (Tamm Dancoff) and the RPA (Random Phase Approximation). In general it is well written and scholarly presented section which allows a reader to briefly get acquainted with pros and cons of various currently used methods for calculation of ground and excited states. However, upon reading the section on very crucial Born-Oppenheimer (BO) approximation (page 2, eq. 1.2.1), I feel that it has been presented too superficially. In my opinion it should be more carefully presented given the fact that in the excited states (processes) such approximation can fail. The more accurate extension of BO, adiabatic approximation is not mentioned at all. It is in fact written that “BO can fail when two potential energy surfaces are close to each other”, but it is still not clear for a reader why it is the case. Furthermore, the author has written that BO “is not good for larger systems”. It is needed to explain this statement in detail since, in my opinion, it is not valid in general. Accordingly, I expect that the candidate will explain both the BO and adiabatic approximation including a discussion on when (and why) such approaches can fail. The independent particle model, which is crucial for the Slater-determinant approximation of many-electronic wavefunction, is also not mentioned at all before the HF section occurs.

The chapter two contains the ERPA and ERPA2 formulas together with the corresponding examples of applications (excitations energies and potential energy curves for H_2 , LiH and N_2). It has been proven that the new variants of the RPA are superior due to geminal-based inclusion of larger amount of (intrageminal)correlation effects. At the same time these approaches scale similarly (or better) as compared to RPA. It is also mentioned, in the case of N_2 , that both schemes perform worse due to lack of intergeminal correlation energy. Such correlation energy has been smartly included in the elegant approach ERPA-GVB (discussed in the chapter 5) – accordingly, are the results for N_2 getting better (than ERPA and ERPA2) when considering the ERPA-GVB ?

In the chapter 3 the performance of strongly orthogonal geminal ansatz is tested for description of excitation energies. The time dependent version of the APSG has been considered (TD-APSG) against the ERPA and ERPA2 schemes. It is shown that ERPA2 and TD-APSG perform better in describing double excitations than ERPA due to inclusion of diagonal double elements. It is found that both ERPA2 and TD-APSG describe correctly excitation energies of dissociating molecules (Li2, BH, H2O). It is also concluded that for larger molecules the accuracy of single excitations around the equilibrium geometry predicted by the TD-APSG method (or ERPA2) will be similar to the RPA. An inspection of the TD-APSG formula (Eq. 3.2.38, page 52) leads to the following trivial question whether eigenvalues (+/-) are always perfectly paired, i.g. are the same absolute eigenvalues always obtained; if so, what could be the origin of such pairing (would it be lost for example for open shell system)?

In Chapter 4 the candidate filled the gap by combining the well-known GVB-PP method (accounting for left/right correlations within the electron pair, used mostly for the ground state properties) with the linear response formulation (giving rise to the TD-GVB approach). It has provided a new tool for analyses of excited states of molecules (especially for stretched bonds), which is also cheaper than previously discussed TD-APSG. It has been tested for ground and excited states of H_2 , LiH and H_2O . A drawback is that at equilibrium geometry (ground state) the TD-GVB performs similarly to the uncorrelated TD-HF.

Finally, as far as the methodological aspect is concerned, a new, elegant and the most powerful (in my opinion) method is proposed in chapter 4, which takes advantage from both the GVB-PP method (accounting for static correlation) as well as the ERPA scheme (containing intergeminal correlation energy). The resulting new ERPA-GVB method, with the balanced treatment of static and dynamics correlation, is capable to describe various systems/processes: energy barriers for the dissociation of F_2 , linearization of H_2O , twisting the double bond in ethylene up to H-migration within the ethylene. The results appeared to be in excellent agreement with more computationally demanding approaches (CCSD(T,Q), FCI, MR-CISD). In my opinion it is the most useful and appealing approach which shall be further explored. It is necessary to point out that the mentioned F_2 molecule has been for long time extremely challenging species (and, in fact, it is still for some of quantum chemical methods). I remember my first adventure with F_2 (in 2003) when I have been trying (based on the typical KS DFT) to obtain an overall bond dissociation energy BDE ($F_2 \rightarrow 2F$). All my DFT attempts badly failed in reproduction of the accurate experimental BDE value (which is 37.5 ± 2.5 kcal/mol, based on accurate mass spectrometry measurements). It is clear now that such seemingly simple species very often need to consider large amount of dynamic correlation in order to be closer to experiment. It has been elegantly demonstrated that the ERPA-GVB nicely capture a “devil”, i.g. the intergeminal correlation effects, what leads to correct dissociation curve as compared with the CCSDTQ. The intrageminal correlation is almost constant. It is reported in Table 5.1 (page 80) that the BDE value for F_2 is 29.8 kcal/mol (ERPA-GVB value). On the other hand it is known that the experimental estimation is quite larger, i.e. 37.5 ± 2.5 kcal/mol – in this respect the ERPA-GVB outcome is even better than the CCSDTQ, but still exhibits notable error. I would like the candidate try to shed some light on this discrepancy of bond dissociation energy (between theory and experiment), which is of course, debatable. One could add, that quite old BOVB (Breathing Orbitals Valence Bond) calculations of Hiberthy (J. Chem. Phys., Vol. 101, No. 7, 1 October 1994) have provided the value of 34.0 kcal/mol, which seems now the closest to the experimental value. Similar is true for the ammonia inversion barrier, which is 5.8 kcal/mol (experimental estimation), whereas the best correlated methods yield 6.8 kcal/mol. Interestingly, the barrier of 5.1 kcal/mol has been already obtained from the HF calculations which contain d-polarization functions (The Journal of Chemical Physics, 1970, 52, 4133).

Another molecule from my list of “DFT-disappointments” is chromium dimer (Cr_2) which is also seemingly simple, but also complicated molecule. It serves now as a truly challenging test for new correlated methods. It contains formally sextuple bond between chromium atoms, what demonstrates the need to account for dynamic correlation. In practice, the CASSCF occupations of the appropriate d-orbitals demonstrates that the real bond order is close to four (due to two very weak δ -delta-contributions). Surprisingly, my recent DFT calculations has shown that the two δ -contributions are indeed very weak (up to 2 kcal/mol). It has further been shown that the PES of Cr_2 is more complicated due to the presence of one deep minim (at 1.6 Å) and the second very shallow pseudo-minimum (at ~2.6 Å). It has been shown recently (J. Chem. Theory Comput. 2016, 12, 1647), that multi-reference DMRG-CASPT2 or DMRG-NEVPT2 are (so far) the best as compared with the experimental value of 35.3 kcal/mol. Given that fact the ERPA-GVB captures large amount of dynamic correlation, I wonder about the candidate opinion on its performance (ERPA-GVB) for Cr_2 dissociation – would it be better or worse and possibly why?

In the previous chapters the new methods have been presented and deeply discussed. In the very last part the candidate has demonstrated his creativity in improving the numerical algorithm for minimization of the energy of APSG wavefunction (which is known to converge slowly due to the need for optimization of both orbitals and expansion coefficients). It has been applied the BFGS (which belongs to a quasi-Newton family) approach in order to

avoid full Hessian determination. Additionally DIIS technique (Direct Inversion in the Iterative subspace) has been also tested. The two variants are analysed: BFGS and BFGS/DIIS. In line with the intuition the latter converges in fewer number of iterations. I am wondering whether it is worth going into optimization methods which must determine Hessian (or its part) or even gradients. Maybe, an alternative, and possibly better solution would be to apply other quite highly developed schemes like genetic algorithms, combined, for example with the neural networks. Such schemes are known to perform fast and quite well quantitatively at least for some optimization problems.

I have not found any information in the thesis about a type of program which has been applied by the candidate for developments/coding – did author write down his own code from the scratch which uses externally the known codes (Gaussian, Dalton, etc.)? Or the necessary modifications have been introduced directly into some existing packages.

Finally, just a comment that all we would like to be able to describe very accurately large systems (e.g. 100 or 1000 atoms including transition metals or extended systems) and their reactivity. I am wondering about the author's future vision on this issue – how correlated methods shall progress in the future toward linear-scaling? Is it reasonable to go into the QM/MM like schemes or maybe semi-empirical treatment of some formulas? I feel that the thesis lacks of such a fragment which would shed some light at which direction correlated methods shall be developed toward better scaling for larger systems.

Minor deficiencies:

- Eq. 1.1.1 xi variables are not defined;
- Page 2, it is written that the Schrödinger equation is “not so easy to solve without approximations”. It shall be more precisely expressed that it is only possible for model cases.
- Page 4 “a viable ways”.

Recommendation

To summarize, the PhD thesis of Koushik Chatterjee is very highly evaluated since it proposes entirely novel methods of quantum chemistry which have been proven to be very useful in description of excited states and bond-breaking processes. The results have been published in five very high quality publications and one book chapter – these achievements are evidently already noted by the scientific community as evidenced from the almost thirty citations of these works. Hence, in my view, all goals have been successfully accomplished. Furthermore, the candidate has shown the following scientific activity: applying for the NCN funds (Preludium grant DEC-2014/13/N/ST4/03990) and participation in local and international conferences (one poster and three talks). Hereby, I declare, without any doubt, that the PhD thesis of Koushik Chatterjee meets all the criteria specified in the Polish Article 13 of the Act of 14th March 2003 (Dz. U. z 2003 r., 65 pos. 595 including all later updates) regarding the scientific titles and degrees. Accordingly, I would like to express my positive recommendation to the Faculty of Chemistry Board of Łódź University of Technology concerning the Mr Chatterjee's admission to further stages of the doctoral procedures. Due to the significant amount of topical results, as well as the overall impressive scientific activity, I put forward a request to the Faculty of Chemistry Board of Łódź University of Technology for distinction of the PhD thesis of Koushik Chatterjee.

Yours Sincerely,



Dr hab. Mariusz Paweł Mitoraj