Methodological Developments in the Theory of Geminals

Tamás Zoboki

Thesis points of the dissertation

Supervisor: Prof. Dr. Péter Surján

Doctoral School of Chemistry

Theoretical, Physical and Structural Chemistry Doctoral Programme

Head of the doctoral school: Prof. Dr. György Inzelt

Head of the doctoral programme: Prof. Dr. Péter Surján

Laboratory of Theoretical Chemistry

Institute of Chemistry

Eötvös Loránd University

2015, Budapest

Background

We would like to introduce the background material of our research and highlight the most important articles that have direct connection to the work presented in this dissertation.

The most important impact on our work was the Interaction of Chemical Bonds article series [1, 2, 3, 4, 5] by Surján et al. Part II. [2] is of outmost importance regarding our work. This article is a solely theoretical paper with no calculations presented. Nevertheless, it is very important from our perspective, the second-order perturbation correction for the dispersive term of the Hamiltonian (which is a central object in our oncoming investigations) appears firstly in this paper. Part V. of the series[5] is mostly about the implementation of the theory presented in part II. Later it turned out that the dispersive term in this theory is the one which causes complications during simultaneous dissociation of bonds in a molecule. Technically this is manifested in the appearance of one or more zero eigenvalues in the A matrix of the below system of linear equations (this system of equations determines the first-order perturbative wave function correction):

$$\sum_i \underbrace{\langle \Psi_j^{(0)} | E^{(0)} - \hat{H}_0 | \Psi_i^{(0)} \rangle}_{A_{ji}} t_i = \underbrace{\langle \Psi_j^{(0)} | \hat{W} | \Psi^{(0)} \rangle}_{d_j} \tag{1}$$

$$\mathbf{At} = \mathbf{d}$$

The main aim of the Coupled Cluster based theory introduced is getting rid of the unwanted divergences.

In [6] Surján and Rosta approach the topic of [5] from a different aspect, namely by pointing out the unusual aspect of this geminal-based perturbation theory: it can be viewed as an application for two-body zeroth order Hamiltonians in multireference perturbation theory. In this article many applications are presented and also the problem initializing our work with a geminal-based Coupled Cluster theory is mentioned explicitly: describing simultaneous breaking of bonds is impossible to describe with this theory due to divergence of the dispersive correction.

The diagrammatical approach in geminal theory was initiated by Paldus et. al [7, 8]. They went as far as expressing the APSG energy equation in terms of diagrams but no further energy corrections have been introduced by them. Nevertheless, their work was the most influential one regarding the description of the diagrams appearing in the Dispersive

Linear Coupled Cluster theory. This theoretical construct is currently an unpublished work of ours.

A stationary property of the APSG wave function

The APSG wave function is non-invariant to the unitary transformation of geminals, this is already stated in the review paper written by Surján [9]. The idea of investigating the effect this has on the APSG energy itself has not been investigated before our work though. In other words, we phrased the following question to ourselves: is it possible to further decrease the APSG energy by finding an appropriate unitary transformation of geminals? To answer this question, the following work was carried out:

1. The energy expression containing two unitary transformed geminals was derived.

2. A computer implementation was written for these formulas in Fortran language.

3. As an application, two sample calculations were performed in 6-311G* basis set. First, the unitary transformation of two hydrogene molecules was taken into account. The four hydrogene atoms were collinear in our numerical example, in the H_2 molecules the distance between the hydrogene atoms was 0.74 Å, while the distance between the molecules was 1.26 Å. The unitary transformation was described by using a two-by-two rotation matrix with a rotation angle parameter (α). We calculated the energy value corresponding to different α values. This curve had minima at orbital rotation angles $\alpha = \{\frac{k\pi}{2} | k \in \mathbb{Z}\}$ and maxima at angles $\alpha = \{\frac{\pi}{4} + \frac{k\pi}{2} | k \in \mathbb{Z}\}$. In this case $\alpha = 0$ is the identity transformation and $\alpha = \frac{\pi}{2}$ refers to the interchange of the two geminals. The curve had an exact minimum at the APSG wave function.

4. The example of two non-equivalent geminals was also studied, calculations for a helium atom and a hydrogene molecule were performed in 6-311G** basis set. The atoms were placed collinearly in these calculations, the H-H bond length is 0.74 Å and the helium atom is placed 1.26 Å far from one of the hydrogene atoms. The APSG energy was not an exact minimum in this case.

5. It was shown analytically that the APSG wave function is not only stationary to the unitary transformation of orbitals, but also to the transformation of the geminals themselves.

Coupled Cluster-type corrections to the APSG wave functions

In the 'Background' section, we have already mentioned the unsatisfactory behaviour of geminal perturbation theory in important chemical processes, in this case the simultaneous dissociation of chemical bonds. The divergence of the potential energy surface observed is a direct consequence of the appearance of values close to zero in one or more rows (and columns) of matrix **A** in eq. (1). In this section we aim at correcting this property of geminal perturbation theory by introducing a Coupled Cluster-type approach. This theory by definition belongs to the family of Multireference Coupled Cluster (MRCC) Theories due to the multireference nature of the APSG wave function. Our related work consisted of the following points:

6. The energy and amplitude equations taking into account only the so called 'dispersive excitations' in the $\hat{T}$ were explicitly derived (both linear and non-linear terms).

7. A Fortran implementation of both the energy and amplitude equations was coded. In this program it is possible to choose between adding the non-linear corrections or omitting them.

8. As including only dispersive excitations in the excitation subspace was not sufficient by itself (only a small decrease in the energy compared to the APSG was obtained), 12 different schemes were introduced depending on what type of excitations are taken into account besides the dispersive ones

9. As a first example, the interaction of two helium atoms was studied. It can be stated that all of the different types of interaction subspaces used were capable of describing the $R \longrightarrow \infty$ case and 6 of them (containing the single and double excitations from the determinants making up the reference and/or single and double excitations from the spin-polarized states) were also able to describe the equilibrium state belonging to the energy minimum. In this respect single and double excitations were definitely needed to correctly describe the potential energy curve from a quantitative point as well. Introducing these states to the interactive subspace, the energy

difference relative to the FCI energy stayed in the 10^{-8} a.u. range for the complete energy curve.

10. For our next example we chose the symmetric dissociation of water, which is a simultaneous stretching of both OH bonds of a water molecule. The H-O-H angle was kept constant during this process ($110.6°$). In our calculations 6-31G basis set and frozen core approximation was applied for the water molecule, this resulted in 4 geminals altogether, the bonding geminals having 4 orbitals in their subsets while non-bonding having only 2. The divergence of the curve calculated by using geminal-based perturbation theory disappears when using the geminal-based LCC thory with only dispersive states included. It is has to be noted though that inclusion of the spin-polarized states was inevitable, otherwise one also arrives at a divergent curve. Nevertheless, a good quantitative description of the dissociation process cannot be obtained just by including the dispersive states in the interacting space, the FCI error falls in the 0.01 a.u range which is not acceptable for a good method.

11. The effect of charge transfer states (single and double excitations of the determinants making up the APSG or its special type, the General Valence Bond wave function) on the water symmetric dissociation was also discussed. The different basis sets used for this purpose were the 6-31G and 6-31G* basis sets. The calculations were restricted to using the GVB reference. From the calculations it was possible to draw the conclusion that in the dissociated region, inclusion of the one-geminal excitations did not have too much effect on the absolute energies (these one-geminal excitations are intrageminal excitations in other words, they consist of a geminal being excited from its ground state to one of its excited states). This trend seemed to be true for the 'transition region' (the set of energy values between the dissociated state and the equilibrium state) as well. Unfortunately most of the interaction subspaces result in a diverging curve in this transition region. The only exception is the calculation with the Dispersive Linear Coupled Cluster Theory and the calculation containing the one-geminal excitations (excited geminal states on only one of the geminals) also besides the dispersive states. In the equilibrium region, these interaction subspaces led to no significant energy gains though. One important difference between the equilibrium calculations and those corresponding to the dissociated state, is that here one-geminal excitations do count, the single and

double excitations from the spin-polarized states are those which do not have too much effect on the outcome of the calculations.

12. Regarding the non-linear corrections, we investigated the dissociation of HF in 6-31G* basis. It can be said that these corrections did not bring in a significant change to the general shape of the potential curve, energy corrections lie in the 10^{-6} a.u. range. In the repulsive region of the potential curve this correction seems to be greater if we consider the absolute value, although there is no observable tendency in the sign of this correction, it is oscillating around 0. As we approach the equilibrium and dissociated region of the energy spectrum, the curve smoothes out and the value of the non-linear correction becomes more predictable.

Diagrammatical approach in corrected geminal theories

In this work we made an attempt at creating a diagrammatical formulation of the Multi-reference Coupled Cluster Theory introduced previously.

13. Diagrammatical forms of the mathematical formulas in both the energy and amplitude equations were written up (both for $M_S = 0$ and $M_S \neq 0$ in case of triplet geminals)

14. The diagrammatical rules were determined connecting the formulas to their graphical equivalent.

Conclusion

The content of the 'A stationary property of the APSG wave function' section was published in [10]. Work concerning the section of 'Coupled Cluster-type corrections to the APSG wave functions' had been published in [11]. 'Diagrammatical approach in corrected geminal theories' contains unpublished results elaborated during the writing process of the dissertation.

Bibliography

Background Literature:

[1] P. R. Surján. *Phys. Rev. A*, 30:43–50, 1984.

[2] P. R. Surján, I. Mayer, and I. Lukovits. *Phys. Rev. A*, 32:748, 1985.

[3] P. R. Surján. *Int. J. Quantum Chem.*, 52:563–574, 1994.

[4] P. R. Surján. *Int. J. Quantum Chem.*, 55:109–116, 1995.

[5] E. Rosta and P. R. Surján. *Int. J. Quantum Chem.*, 80:96–104, 2000.

[6] E. Rosta and P. R. Surján. *J. Chem. Phys.*, 116:878–890, 2002.

[7] J. Paldus. *J. Chem. Phys.*, 57:638–651, 1972.

[8] J. Paldus, S. Sengupta, and J. Čížek. *J. Chem. Phys.*, 57:652–666, 1972.

[9] P. R. Surján. *Topics in current chemistry*, 203:63–88, 1999.

Publications supporting the thesis:

[10] T. Zoboki and P. R. Surján. *J. Math. Chem.*, 49:1217, 2011.

[11] T. Zoboki, Á. Szabados, and P. R. Surján. *Journal of Chemical Theory and Computation*, 9:2602, 2013.