Report

Background

In the single-reference(SR) coupled-cluster(CC) theory[1, 2] the wave function is described in terms of an exponential ansatz of interacting clusters of electrons,

$$|\Psi\rangle = \mathrm{e}^{\hat{T}}|0\rangle, \tag{1}$$

where operator $\hat{T}$ is the cluster operator containing the wave function parameters as coefficients of the allowed excitation operators and $|0\rangle$ is the reference determinant which defines the occupied and virtual orbitals. In the most frequently used CC method the excitation rank of the amplitudes is restricted to the singles and doubles (CCSD)[3]. In this case when operator $\hat{T}$ acts on the reference determinant, all the singly and doubly excited determinants appear with respect to $|0\rangle$. These excited determinants form the interacting subspace Q. The CC correlation energy is determined from the Schrödinger equation projected to the reference determinant,

$$\Delta E = \langle 0|(\hat{H}_N e^{\hat{T}})_c|0\rangle, \tag{2}$$

where $\hat{H}_N$ is the normal-ordered Hamiltonian[4] which is identical with the $\hat{H} - \langle 0|\hat{H}|0\rangle$ difference, and subscript c indicates that only the connected part of the above expression should be taken into account. To obtain equations for the unknown CC coefficients the Schrödinger equation is multiplied by $e^{-\hat{T}}$ and projected against the subspace Q. In the CCSD case it reads as

$$\langle 0_{i_1}^{a_1}|(\hat{H}_N e^{\hat{T}})_c|0\rangle = 0, \tag{3}$$

$$\langle 0_{i_1 i_2}^{a_1 a_2}|(\hat{H}_N e^{\hat{T}})_c|0\rangle = 0, \tag{4}$$

where $|0_{i_1}^{a_1}\rangle$ and $|0_{i_1 i_2}^{a_1 a_2}\rangle$ are the singly and doubly excited determinants wrt the reference determinant $|0\rangle$ and the virtual (a_1, a_2) and the occupied $(i_1,\ i_2)$ one-particle indices define the excitation. These are called the fixed indices. The reference determinant and the singly and doubly substituted Slater determinants together form an orthogonal many-electron basis. Utilizing the orthogonality and the normal-ordered form of the second-quantized operators it is possible to introduce a diagrammatic representation[4, 5] which helps the derivation and the efficient implementation of the CC equations.

The aim of the project I worked on in the past years within the confines of the project (grant No. PD108451) supported by the Hungarian Scientific Research Fund(OTKA) was to develop methods and tools to extend the applicability of the above briefly introduced SRCC theory for chemical problems where the wave function has multi-reference(MR) character. The proper generalization of the SRCC method to the MR case is still an open problem. The complexity of this task is well demonstrated by the large number of models introduced in this field (for more details see the reviews in this topic, e.g., Refs. [6–9]).

The main component of the scientific proposal of my project was to strictly retain the orthogonality of the SRCC framework and choose an orthogonal MR many-electron basis which suits for the chemical problem under investigation and use it as a basis for a CC expansion just like the ordinary Slater determinants are used in the SRCC. To that end a one-particle labeling is introduced for the MR basis elements as an analogue of the indices of determinants in Eqs. (3-4). The MR functions with the determinant-like labeling form a basis where a CC method can be defined in a similar manner known from the SR theory. The concept of the originally proposed MRCC method were connected to a unitary transformation, which rotates each determinant to the MR function holding the same label. The original plan was to fix the MR basis in advance (as the eigenfunctions of the active part of the Hamiltonian) then define the labeling, but we could not find a good definition for the labeling which would be applicable for complex potential energy surfaces(PESs).

In the following sections the results originated from the above idea and other outcomes of the projects are discussed.

Results

Quasiparticle-based MRCC theory

The first significant improvement on the theory is to drop the concept of the predefined MR basis and fix first the unitary transformation which naturally defines the MR basis as well. For the definition of the unitary transformation we can suppose that it is parametrized in an exponential form. The number of the possible unitary transformations is infinitely large, but we can restrict ourselves to those which connect a predefined 'formal' Fermi-vacuum to the reference complete active space (CAS) function. We can also suppose that the unitary transformation contains exclusively active indices and the connection of the reference function and the formal Fermi-vacuum uniquely determines the parameters of the unitary transformation. This can be easily done if the form of the transformation is identical to the exact wave operator of the unitary CC approach[10, 11] restricted to the active space. Apart of its simplicity, this definition has some other advantages, namely, this unitary transformation is a connected quantity ensuring the extensivity of the whole method and for those cases where the wave function is single determinant dominated, the unitary transformation is close to the identity thus the calculated energy will be also close to the SRCC result. Using the above unitary transformation (or any other definitions) it is possible to introduce a set of quasiparticles. These are second-quantized creation and annihilation operators which satisfy the fermion anticommutation rules. These operators allow us to represent the CAS reference function and any other elements of the MR basis as determinants of quasiparticles in a second-quantized form. Since the mathematical structure of the new MR framework is basically equivalent to that of the SR case, the tools like the operator contractions, normal-ordered operator products, Wick's theorem, diagram technique, *etc.* can be straightforwardly generalized to the MR case. This MR normal-ordering approach is a possible alternative of the one previously published by Mukherjee and Kutzelnigg[12, 13].

The MRCC theory introduced in my scientific proposal has been reformulated using the quasiparticles. For the first sight the novel MRCC equations have the same form than that of the SRCC method in Eqs. (1-4). The most peculiar difference with respect to the SR case is the more than two-particle nature of the Hamiltonian in the new representation. The new form of the theory and the analogy with the SRCC allow us to discuss various qualitative properties (size-consistency, extensivity, invariance for special orbital rotations) of the method in a transparent way.

The method has been implemented in a full configuration interaction-based code to test the performance of the new unitary transformation. This implementation is an inefficient one, but allow us to perform calculations for small model systems and its simplicity helps the fine-tuning the new model.

Even though the quasiparticle-based MRCC (QMRCC) method is an inherently MR approach, the performed test calculations indicate that at the singles and doubles level of theory it gives little if any correction with respect to the SRCC results and at least the restricted triple (QMRCCSDt) or the restricted triple and quadruple amplitudes (QMRCCSDtq) are needed to obtain accurate results. Although we could not avoid the application of certain triple and quadruple amplitudes, we could make some improvement with respect to the SR-based MRCC (SRMRCC) method, where the exponential wave function is similarly parametrized[21, 22]. Firstly, we have observed faster convergence of the accuracy with the level of the approximation compared to the SRMRCC case, secondly, the convergence of the CC calculations are also improved with respect to the SRMRCC case due to the more accurate CAS function used as the reference in the QMRCC case.

The QMRCC method (with the unitary transformation we recently using) has a drawback common with the SRMRCC method, namely, both methods depend on the applied formal Fermi-vacuum. Note that, in the QMRCC case this dependence is reduced as the reference is a MR CAS function and only the basis of the interacting subspace is Fermi-vacuum dependent. The Fermi-vacuum is usually the determinant with the largest contribution to the reference CAS function. The problematic nature of this Fermi-vacuum dependence can be easily understood in those cases where along a PES the leading determinant of the CAS is changed. Since generally there is no single determinant that is optimal for all the geometries one can use, for example, the one with the largest contribution at each geometry point and put on with the discontinuities on the PES. To avoid these undesirable artifacts we tested two possible solutions. Our first attempt was to use a symmetry breaking unrestricted Hartree-Fock function as a formal Fermi-vacuum, which can provide a smooth description for the whole PES at a single-determinant level. Although in this way we can obtain smooth PESs with the QMRCC, but for the complicated regions we loose the spin- and spatial-symmetries of the wave function. It is not only a theoretical problem but also a practical drawback as due to the lack of the proper description of symmetries at quasi-degenerate situations the convergence of the CC calculations might be rather problematic. To avoid the loss of the symmetries we are also investigating a Jeziorski–Monkhorst-like(JM)[14] wave function ansatz, where the exponential wave functions are determined with respect to each determinant having large component at a region of the PES and the linear combination of these functions are used where the linear coefficients are determined from the variational principle.

The above results are published in the Journal of Chemical Physics[15]. As a consequence of the complexity of the QMRCC method, the implementation, the debugging process, and the steps to achieve a more or less optimal performance of the new code took longer than I expected and the efficient QMRCC code is still incomplete.

A second-order MR perturbation theory

Similarly to the SR case, where the CC approach is closely related to the second-order many-body perturbation theory, we could derive a low cost perturbative alternative to the QMRCC theory. As a by-project of our MRCC investigations, using some components of the determinant-based QMRCC code a second-order perturbation theory has been implemented using the quasiparticle framework. The definition of the new theory strictly follows the form of the single-reference many-body perturbation theory and retains several of its beneficial properties like the formal simplicity, robustness against the intruder problem, and the extensivity. To investigate the accuracy of the new method test calculations have been performed on typical MR model systems like the dissociation process of the HF molecule, the symmetric dissociation of the water molecule, and the perpendicular insertion reaction of Be to H_2 to form the BeH_2 molecule. The results are compared to that of the second-order CAS-based PT (CASPT2)[16, 17] and second-order n-electron valence state perturbation theory (NEVPT2)[18, 19]. According to these results the accuracy of the quasiparticle-based perturbation theory is similar to the accuracy of the NEVPT2.

The main disadvantages of the quasiparticle-based MBPT are the lack of invariance to the rotation of active orbitals and the high calculation cost of intermediate quantities for large CAS problems wrt the NEVPT. In the published paper[20] the efficient implementation of the method is also discussed.

Efficient implementation of the active-space CC methods

To be able to use the QMRCC approach or any approximation of the original theory for practical calculations an efficient implementation of the approach is required. As this approach is closely related to the SRMRCC method, which has a simpler structure, it was transparent to start with an efficient implementation of the SRMRCC. At the start of the work an SRMRCC code were available for us, previously written by Kállay[23]. As in this implementation the calculation of diagram contractions are not properly vectorized, I decided to write a new code where the amplitude-intermediate contractions are calculated as matrix-matrix products. Another motivation behind the new implementation is to have a code where the active indices of the amplitudes and intermediates are separately treated as it suites for the development of the QMRCC theory.

The new implementation partly based on the application of strings, strings of fixed indices. The fixed indices are those one-particle indices which label the element of the CC equations at Eqs. (3-4). The indices of fixed active lines belonging to amplitude or intermediate diagrams are not treated individually but as part of strings (ordered list of one-particle indices). The rest of the lines are labeled by one-particle indices which allows the efficient evaluation of contractions using the dgemm routine.

For the derivation and implementation of the SRMRCC equations a new diagrammatic approach is introduced where the diagrams contain one-particle and also string lines. It is important to note these diagrams are more than useful notations, these are mathematical object with a fix ”value” which can be evaluated using the diagram rules[4, 5]. As our new diagrams contain string lines the diagram rules needed to update accordingly. Using the diagrams with string lines the CC equations can be represented in an excitation level independent form. This CC representation can be adapted to the SRMRCC case, where using the new approach the working equations were derived and implemented in an excitation independent form. As the number of the applied intermediates is still large (several hundreds) automated code generator techniques were used.

To obtain a relatively compact and excitation independent, hard-coded program package some simplifications were used in the derivation of MRCC equations which works well when the list of strings is short but it is inefficient if this list is significantly longer than the number of virtuals. This might be seen as a strong restriction, but considering that the SRMRCC method is not the method of choice for large CAS problems, this can be a reasonable compromise.

Due to the applied simplifications the new SRMRCC code is optimal for small CAS problems, while for larger CAS spaces the improvement is moderate. Accordingly, as the test results show the new code is currently rather efficient for small, 2 by 2 and 4 by 4 CAS problems (the speedup is in the order of 10) but not significantly better than the previous implementation for larger CAS calculations.

It is worth to note that the innovations behind the new code also increases the applicability of the other active-space CC methods[24–33]. We can also mention that the new CC code is able to perform SRCC calculations at arbitrary excitation levels supposing that each orbital is active, but in its recent form it is inefficient. In the current implementation we supposed that the number of strings are relatively short, but for the efficient application of the new framework for the high-order SRCC case this condition needs to be relaxed.

The manuscript of this study is submitted to the Journal of Chemical Physics. The manuscript is available at https://drive.google.com/drive/folders/0B1jt1HV-mZxmVGlqTHNLQnZhRTQ?usp=sharing as long as it is not officially published.

A novel Jeziorski–Monkhorst MRCC ansatz

The JM ansatz[14] is a seemingly straightforward generalization of the SRCC approach where an exponentially parametrized function is defined for each relevant determinants (model determinants) and the wave function is found as the linear combination of these functions. As generally a given determinant of the interacting subspace can be reached from more than one model determinants using the exponentially parametrized excitations, the number of parameters of the JM ansatz is larger than the number of equations obtained by projecting the Schrödinger equations against the determinants of the interacting subspace. This redundancy problem can be solved either by eliminating redundant parameters[34, 35] or adding a set of sufficiency conditions to have enough equations as it is done in Mukherjee's state-specific MRCC (SSMRCC) theory[36–38]. The SSMRCC method formally has many appealing features like the extensivity and a relative simplicity but it turned out that it is numerically unstable and inaccurate[7, 39, 40]. A possible source of the inaccuracy is that the SSMRCC does not fulfill the proper residual condition, i.e., the SSMRCC wave function does not fulfill the Schrödinger equation in the subspace of the projection manifold which is used to obtain the CC coefficients (in the SRCC case this manifold contains the $\langle 0^{a_1\ldots a_n}_{i_1\ldots i_n}|e^{-\hat{T}}$ functions).

In the last year I developed a JM MRCC ansatz—where with the properly chosen model determinants and cluster amplitudes—the redundancy problem can be avoided. As the large number of MRCC approaches shows, it seems that the CC-like parametrization does not fit for the description of active electrons and active excitations. In the new approach the active excitations are linearly while the inactive excitations are exponentially parametrized. To completely cover the usual MRCC/MRCI interacting subspace the model space is a larger set than the CAS determinants of the given problem, namely, for an n electrons CAS problem it contains determinants with n, $n \pm 1$, $n \pm 2$, *etc.* active electrons. As the novel JM MRCC approach satisfies the proper residual condition, we can expect more accurate results. The new approach has been implemented for two-by-two CAS problems by modifying the pilot implementation of the QMRCC model. The first numerical tests reveal that our initial concept to choose the model determinants leads to numerical instabilities as some of the model determinants have too small coefficients. The solution of this problem is recently in progress.

The manuscript of this study is incomplete at the time this report is finalized. The current version of manuscript can be also found at https://drive.google.com/drive/folders/0B1jt1HV-mZxmVGlqTHNLQnZhRTQ?usp=sharing .

Summary

The main results of the project entitled ”Development of multi-reference coupled-cluster methods” is as follows. A new MRCC method is developed using the concept of quasiparticles where these objects are defined by a unitary transformation of the N-electron space. In the new framework an alternative definition to the normal-ordering is obtained suitable for MR problems. The new method is implemented for test purposes. Using the new code we found that without applying the restricted higher-order excitations, known from the SRMRCC model, the method is inaccurate. Further numerical tests raveled that the new approach shows a faster convergence to the correlation energy than the SRMRCC with the increasing excitation level. Using the quasiparticle framework a MR second-order perturbation approach is also developed and investigated.

To achieve the efficient implementation of the QMRCC approach a second set of programs is also written. To support this work a new diagrammatic technique is developed where the CC diagrams contain lines labeled by string indices in addition to the one-particle labeled lines and the diagram rules are extended accordingly. The new diagrams allow a compact, excitation level independent representation of the CC equation. The new code considerably improves the applicability of the SRMRCC method and other active-space CC approaches and provides a basis for the efficient QMRCC code. The new approach has the potential to be applicable for the higher-order SRCC calculations as well.

Finally, a new redundancy-free JM ansatz-based MRCC theory is also developed which fulfills the proper residual condition. The pilot implementation of the new approach is prepared with some modification of the determinant-based QMRCC code.

References

[1] J. Čížek. *J. Chem. Phys.*, 45:4256, 1966.

[2] J. Čížek. *Adv. Chem. Phys.*, 14:35, 1969.

[3] G. D. Purvis III and R. J. Bartlett. *J. Chem. Phys.*, 76:1910, 1982.

[4] I. Shavitt and R. J. Bartlett. *Many-body Methods in Chemistry and Physics*. University Press, Cambridge, 2009.

[5] J. Paldus and J. Čížek. *Adv. Quant. Chem.*, 9:105, 1975.

[6] P. Piecuch. *Mol. Phys.*, 108:2987, 2010.

[7] L. Kong. *Int. J. Quantum Chem.*, 109:441, 2009.

[8] A. Köhn, M. Hanauer, L. A. Mück, T.-C. Jagau, and J. Gauss. *WIREs Comput Mol Sci*, 3:176, 2013.

[9] R. J. Bartlett and M. Musiał. *Reviews of Modern Physics*, 79:291, 2007.

[10] W. Kutzelnigg and S. Koch. *J. Chem. Phys.*, 79:4315, 1983.

[11] R. J. Bartlett, S. A. Kucharski, and J. Noga. *Chem. Phys. Lett.*, 155:133, 1989.

[12] D. Mukherjee. *Recent Progress in Many-Body Theories*, 4:124, 1995.

[13] W. Kutzelnigg and D. Mukherjee. *J. Chem. Phys.*, 107:432, 1997.

[14] B. Jeziorski and H. J. Monkhorst. *Phys. Rev. A*, 24:1668, 1981.

[15] Z. Rolik and M. Kállay. *J. Chem. Phys.*, 141:134112, 2014.

[16] K. Andersson, P. Malmquist, B. O. Roos, A. J. Sadlej, and K. Wolinski. *J. Chem. Phys.*, 94:5483, 1990.

[17] K. Andersson, P. Malmquist, and B. O. Roos. *J. Chem. Phys.*, 96:1218, 1992.

[18] C. Angeli, R. Cimiraglia, S. Evangelisti, T. Leininger, and J.-P. Malrieu. *J. Chem. Phys.*, 114:10252–10264, 2001.

[19] C. Angeli, R. Cimiraglia, and M. Pastore. *Theor. Chim. Acta*, 117:743, 2007.

[20] Z. Rolik and M. Kállay. *Theor. Chim. Acta*, 134:143, 2015.

[21] N. Oliphant and L. Adamowicz. *J. Chem. Phys.*, 94:1229, 1991.

[22] P. Piecuch, N. Oliphant, and L. Adamowicz. *J. Chem. Phys.*, 99:1875, 1993.

[23] M. Kállay, P. G. Szalay, and Péter R. Surján. *J. Chem. Phys.*, 117:980, 2002.

[24] P. Piecuch, S. A. Kucharski, and R. J. Bartlett. *J. Chem. Phys.*, 110:6103, 1999.

[25] P. Piecuch and L. Adamowicz. *J. Chem. Phys.*, 100:5792, 1994.

[26] L. Adamowicz, P. Piecuch, and K. B. Ghose. *Mol. Phys.*, 94:225, 1998.

[27] J. Shen and P. Piecuch. *J. Chem. Phys.*, 136:144104, 2012.

[28] J. Shen and P. Piecuch. *J. Chem. Theor. Comp.*, 8:4968, 2012.

[29] K. Kowalski and P. Piecuch. *J. Chem. Phys.*, 113:18–35, 2000.

[30] S. Das, M. Kállay, and D. Mukherjee. *J. Chem. Phys.*, 133:234110, 2010.

[31] J. Olsen. *J. Chem. Phys.*, 113:7140, 2000.

[32] A. Köhn and J. Olsen. *J. Chem. Phys.*, 125:174110, 2006.

[33] L. K. Sørensen and J. Olsen. *Mol. Phys.*, 115:90, 2017.

[34] W. D. Laidig and R. J. Bartlett. *J. Chem. Phys.*, 104:424, 1984.

[35] M. R. Hoffmann and J. Simons. *J. Chem. Phys.*, 88:993, 1988.

[36] U. S. Mahapatra, B. Datta, B. Bandyopadhyay, and D. Mukherjee. *Adv. Quant. Chem.*, 30:163, 1998.

[37] U. S. Mahapatra, B. Datta, and D. Mukherjee. *Mol. Phys.*, 94:157, 1998.

[38] U. S. Mahapatra, B. Datta, and D. Mukherjee. *J. Chem. Phys.*, 110:6171, 1999.

[39] M. Hanrath. *J. Chem. Phys.*, 128:154118, 2008.

[40] S. Das, D. Mukherjee, and Mihály Kállay. *J. Chem. Phys.*, 132:074103, 2010.