Multi-reference many-body perturbation and coupled cluster developments

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Multi-reference many-body perturbation theory and coupled cluster developments

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Abstract

Multi-reference methods for the description of quasi-degenerate ground states and excited states of many-electron systems have been one of the main objectives of scientific activity at the Quantum Theory Project (QTP) University of Florida in Gainesville. The pioneering works by Dr. Per-Olov Löwdin on the partitioning technique, important contributions to the development of multi-reference methods made by Dr. Monkhorst and Dr. Bartlett must be mentioned here. Dr. Bartlett, his group and its visitors have been especially active in this field. In this paper we would like to describe some of multi-reference developments, problems that have been faced and solved as well as those which still require solving. The focus is on multi-reference many-body perturbation theory and coupled-cluster approaches. We present recent advances and future perspectives in the development of these methods. A special attention is paid to two multi-reference approaches that seem very promising and have been either initiated or developed at QTP.

1. Introduction

Single-reference many-body perturbation theory and coupled-cluster methods [1] have proved very successful in describing many-body systems [2]. The limitation is that they perform very well when the wave function is dominated by a single determinant but when more determinants than one are significant in the wave function, i.e. we have to deal with quasi-degenerate situation, then truncation schemes used in single-reference (SR) methods may not be any longer efficient [3]. The reason is that the truncation schemes are usually based on the SR perturbative analysis of wave function contributions which validity is basically restricted to SR cases. For example, the basic computational schemes for SR configuration interaction (CI) and coupled-cluster (CC) methods include double excitations with respect to the reference determinant which contain the lowest first-order terms. In quasi-degenerate situations this may not provide sufficiently accurate results since the perturbation expansion does not converge fast and higher-order contributions become significant. To increase the accuracy excitations of higher than first order can be included and that concerns, first of all, triple excitations since the single ones are usually incorporated in the basic approximate approaches together with doubles. The full inclusion of triples makes the computational CC scheme numerically demanding [4] so to arrive at CC formulations that are computationally attractive an approximate estimate of the effect of triples must be considered. Two options are possible here, modification of the CC equations for connected doubles in which contributions from connected triples are presented through the lowest-order terms [5] or construction of a posteriori corrections to the CC with singles and doubles energy (CCSD) [6, 7]. They represent iterative and noniterative approaches to the problem, respectively. Again, perturbative arguments used in both cases are of limited validity in the presence of quasi-degeneracy so the effectiveness of evaluation of connected triples in this way is rather restricted to the case when the degree of quasi-degeneracy is rather low.

It was clear that an extensive development of the single-reference approaches could not be effective and CC schemes with the full inclusion of triples [4], quadruples [8] or even pentuples [9] have been mainly employed in benchmark calculations. To treat situations when more than one determinant dominate the wave function a different strategy is necessary, namely

these determinants should be treated on the same footing in the expansion. Thus they should be all used as references for selecting contributions to the wave function. According to this strategy the single-reference expansions with singles and doubles (SD) should be extended to include also single and double excitations with respect to other dominant determinants since this is more effective than to increase the excitation rank in the SR approaches.

The idea of replacing single reference with a set of reference determinants leads to multi-reference (MR) formulations of methods designated for description of many-body systems. There was a hope that with more general formalisms it would be possible to overcome limitations of the single-reference approaches and obtain methods of universal applicability. Unfortunately generalizations of the most advanced methods such as perturbation theory (PT) and CC method turned out nontrivial. The problem is that in multi-reference cases we have to deal with two types of electron correlation, nondynamic and dynamic, that must be treated in different ways. The first type is associated with the strongly interacting reference determinants. The second one gives contributions to the wave function from the space orthogonal to that spanned by the reference functions. The wave function must include all reference determinants while the complementary space contributions should be incorporated in an approximate yet, as much as possible, effective way. Obviously, we would like to have them expressed through some kind of perturbation or coupled cluster expansion.

The multi-reference strategy can be easily implemented within the configuration interaction framework. The reason is that both the reference and outer space contributions appear in the wave function linearly so there is no difference in determining them. Thus the multi-reference generalization of CI is conceptually simple and straightforward. Some additional techniques like graphical unitary group approach (GUGA) have been developed [10] to make MR-CISD calculations simpler and more efficient. The only difference, compare to the SR case, is that now the eigenvalue problem of matrix representation of the Hamiltonian in a space spanned by reference determinants and determinants that are singly or doubly excited with respect to at least one them must be solved. Due to its simplicity MR-CISD is one of few methods that are used in routine calculations requiring a MR description. The disadvantages of MR-CISD are lack of size-extensivity and relatively poor description of dynamic

correlation.

The MR generalizations of many-body perturbation and CC theory are quite complicated and there are several reasons for that. First both types of correlation effects are treated differently in the expansion. Nondynamic correlation must be represented exactly in the wave function, i.e, through linear combination of the reference determinants while for the dynamic part truncated perturbation or coupled cluster expansions are assumed. It becomes clear that unlike MR-CISD this calls for a two-step procedures. There are two options that can be considered which differ in the order of determination of these effects. One can try to evaluate the nondynamic correlation first and then the impact of dynamic correlation on the energy. In such a case diagonalization of the Hamiltonian in the reference (model) space is performed first. Frequently the complete active space self consistent field (CAS SCF) method is used here. The orthogonal space contributions are assumed to be responsible for dynamic correlation and they are generated from the first order wave function obtained in the first step. These contributions are given by excitation (substitution) operators replacing occupied spin orbitals with unoccupied ones. Since some spin orbitals that are occupied in one reference determinant can be unoccupied in another one then such excitations can lead to linear dependencies. These linear dependencies must be then removed and that makes such an approach complicated and difficult to analyze. The advantage is that such schemes are quite similar to the SR ones. There are some examples of methods based on this idea like, contracted CI method [11] and a number perturbative approaches [12, 13] with the CAS second-order perturbation theory (CASPT2) being probably most known and popular [13]. The CC schemes can be hardly formulated within this framework and only an attempt to derive and implement a linear version of MR-CC method of this kind has been made [14]. The reason is that cluster operators should be defined as second-quantized operators and for that Fermi vacuum or vacua must be defined. Such a definition introduces a unique classification of spin orbitals into occupied and unoccupied. The second option in formulating the two-step procedures is to evaluate the dynamic correlation first. To do this the effective Hamiltonian technique is used [15, 16]. The so-called wave operator is introduced to give the exact wave function while acting on a linear combination of the reference determinants with

coefficients to be determined in the second step. The second step consists of construction of the effective Hamiltonian, which depends on the wave operator, and its diagonalization. The effective Hamiltonian acts within the reference space and its eigenvalues constitute a subset of eigenvalues of the Hamiltonian. The effective Hamiltonian technique allows us description of several states at a time. That makes the calculation numerically demanding and can be seen as a drawback of the formalism. Within the effective Hamiltonian framework there is a possibility to introduce Fermi vacuum to define excitation operators from reference determinants to the orthogonal complement of the reference space. Unfortunately unlike the SR case there is no obvious choice for the vacuum and basically two strategies can be followed. The first one is to have one Fermi vacuum for excitations from all reference functions, the other is to use each reference determinant as a Fermi vacuum while defining excitations out of it. The two strategies lead to two formulations of the MR many-body perturbation theory (MR-MBPT). The first has been introduced by Brandow [17] while the second one by Hose and Kaldor [18].

As in the SR case the MBPT analysis of the wave operator can show an exponential structure of the expansion. Although the CC methods can be formulated without references to any kind of perturbation expansion they are frequently interpreted as approaches in which certain types of perturbative contributions to the wave function are summed to the infinite order. Thus with each of the two MR perturbation theory formulations, Brandow and Hose-Kaldor type, the corresponding CC expansions can be associated. The one that assume single Fermi vacuum to define cluster operators has been developed over many years with the most fundamental contributions given by Offermann, Ey, and Kümmel [19], Lindgren [20], and Mukherjee [21]. The most important concepts that have been introduced is the normal-ordered form of the exponential expansion [19, 20] and valence universal strategy of solving the CC equations [21]. The method is known as valence-universal (VU) or Fock-space (FS) CC method. The second CC approach with cluster operators associated with different references has been proposed by Jeziorski and Monkhorst [22] and is called the state-universal (SU) or Hilbert-space (HS) CC method.

The other aspect that should be discussed here is the problem of size-extensivity of MR

methods. The property is understood as a proper scaling of the energy with the number of particles. In the SR case size-extensivity can be associated with the connected diagram (term) theorem meaning that the energy is expressed through connected diagrams only. In MR approaches the situation is more complicated because of the two-step procedure employed and both steps should be analyzed as a potential source of size-inextensivity. A direct consequence of size-extensivity of a method is that the energy calculated for a supersystem consisting of two noninteracting subsystems is the sum of energies separately calculated for each of the subsystems. It has been found that diagonalization of the effective Hamiltonian can introduce size-extensivity error [23]. It was clear that as long as the reference space is complete diagonalization of the effective Hamiltonian should not hurt size-extensivity so such an assumption is usually made. More general reference spaces have been postulated in some cases but the one that has been quite widely applied is the quasi-complete space introduced by Mukherjee et al. [24] and Lindgren [25] for excitation energy calculations.

Finally problems that occur in practical applications should be mentioned. First of all selection of the reference space can be difficult in many cases. One of the requirements is that the reference space choice should lead to a clear separation of nondynamic and dynamic correlation effects otherwise the wave operator may have to deal with a significant contribution of nondynamic correlation and then problems with converging iterative procedures for solving the CC equations can occur. Jacobi-type perturbative schemes are especially vulnerable to improper selection of the reference space [26, 27]. The other problems, the multi-reference CC methods are plagued with, are intruder states and multiple solutions [26, 27, 28, 29, 30]. That means that there can be some other state that interferes with the set of states we describe or that iterative schemes provide us with other solution of the CC equations than the desired one.

In the paper we would like to present recent attempts to obtain reliable and efficient methods capable of describing quasi-degenerate states. We start with the single reference approaches that have been modified to handle even a substantial degree of quasi-degeneracy. Also schemes combining SR and simple MR methods are included in this category. Next we discuss recent developments in the genuine MR-PT and MR-CC approaches with the main

2. Extension of applicability of single-reference approaches to multi-reference cases

The method that is usually used to judge the significance of different contributions to wave function is the perturbation theory. The analysis shows that the most important part of electron correlation comes from double excitations. These can be easily supplemented with single excitations constituting the basic schemes with singles and doubles. Single and double excitations can be included linearly in the expansion or in the exponent which leads to the CISD and CCSD methods, respectively. When some degree of quasi-degeneracy is present then the perturbation expansion is not fast convergent and higher-order contributions must be included to maintain the same level of accuracy. These are, first of all, triple excitations but, since the computational cost of their full inclusion is high, their approximate influence on the energy through a posteriori corrections is evaluated within the CC framework. The inclusion of the lowest fourth-order contribution from triples leads to a scheme known as CCSD+T(CCSD) or CCSD[T] [6]. That can definitely improve the CCSD results when quasi-degeneracy is rather weak but the scheme breaks down completely when it becomes stronger. Inclusion of the fifth-order contribution do not help much so clearly SR perturbative arguments are not valid any more in such a situation and should be abandoned. As a result of many calculations it has been established that a reliable improvement is given by a combination of the CCSD[T] correction with one specific fifth-order term. That constitutes the CCSD(T) method [7] that has been broadly used in quantum chemical calculation allowing us, for example, quite reliable description of near equilibrium region in many molecular systems. It should be mentioned that some quadruple corrections have also been proposed like CCSDT(Q_f) and CCSD(T Q_f) [31, 32].

The success of CCSD(T) has inspired some research activity towards extending applicability of a posteriori corrected truncated CC schemes even further. New schemes have been derived using the method of moments [33]. The method allows us to obtain a for-

mula that gives a relation between the exact energy and the energy of a given truncated CC method provided the exact wave function is available. In practice the exact function is replaced by that obtained from the truncated CC calculation. A characteristic feature of the resulting corrections to the CC energies is the presence of renormalization denominators. Thus, depending on the scheme, corrections derived in this way are called the renormalized (R) or completely renormalized (CR) [34]. The basic types are known as R-CCSD(T) and CR-CCSD(T) [34]. It has been shown that such corrections can be easily found by allowing the energy to relax while deriving standard CCSD(T) correction so the method of moments is not really necessary to obtain them [35]. Currently the CR-CC(2,3) correction seems most reliable [36], however, we should be aware that cluster amplitudes that are used to calculate the corrections can be really large in quasi-degenerate situations thus terms that are neglected within some particular scheme are not negligible and, if included, can change the results significantly [37].

Methods mentioned above are of completely single-reference character meaning that they do not use a concept of the reference space. The CC methods that are basically single-reference but employ the idea of reference space are the state-specific MR-CC methods [38]. They can be described as the CCSDT or CCSDTQ methods in which, to reduce the size of the problem, only most important triple and quadruple excitations are included. These are those which represent single or double excitations with respect to other reference determinants. Thus both the nodynamic and dynamic correlation are described through the cluster operator which can lead to large values of the cluster amplitudes. The recent abbreviations for the methods are CCSDt and CCSDtq which indicate that only selected triples and quadruples are included in the schemes.

The other approaches we would like to mention here are based on the MR-CISD method. As mentioned in the introduction the MR-CI method retains formal and computational simplicity of its single-reference counterpart. Hence, the idea of using the MR-CISD scheme as a reliable source of information about nondynamic correlation and combine this with some SR ideas seems very appealing. As in the SR case one may try to introduce the effect of higher excitations than those included in MR-CISD through Davidson-type corrections

[39, 40, 41]. Of course the MR-CISD method is much more difficult to analyze than the SR one so simple generalizations of the SR a posteriori corrections have been introduced without any deeper justification. Thus the Bruna-Peyerimhoff-Buenker correction can be viewed as an extension of the Davidson correction to the MR case [42, 43] and the same has been done for two SR particle-number-dependent corrections [40, 41]. The other way of introducing the effect of higher excitations into the CI scheme that is known from the SR-CISD method is to modify the renormalization term to include only irreducible contributions i.e. those which are not canceled out when quadruple excitations are included. These methods are known as coupled electron pair approximations (CEPA) and several types of them have been developed [44]. The CEPA methods include only the so-called exclusion principle violation (EPV) terms and different types of CEPA include them to a different extent. This idea is difficult to apply within the MR-CISD scheme directly so it is convenient to introduce averaged evaluation of the EPV terms that has been done for the particle-number-dependent size-extensivity corrections to SR-CISD. Two corrections of this kind gave rise to two MR CEPA tapes methods: the MR average coupled pair functional (MR-ACPF) [45] and the MR averaged quadratic coupled cluster (MR-AQCC) [46]. They associate simple particle number dependent factors with the renormalization term in the MR-CISD equations. In spite of the fact that the factors are basically derived in the single reference context and thus can be considered as a very rough estimate of the effect of inclusion of higher excitations, both methods perform quite well in numerical applications.

The next category of methods we would like to concentrate on also combines MR-CISD with single-reference approaches. This type of methods have been initiated by Stolarczyk who proposed to introduce an information about nondynamic correlation into the SR-CC scheme from some simple but reliable external method [47]. He considered the CAS SCF method to be a good source of such an information. To be able to extract this information one of the determinants appearing in the CAS SCF function must be used as a single reference, all the others are treated as singly, doubly etc excited with respect to it. Such a reinterpretation of the CAS SCF function allows us to compare the method with other single reference methods like for example with the SR CC method. The linear CAS SCF expansion can

now be equivalently expressed as an exponential one in the active space with the cluster amplitudes calculated from the CAS SCF coefficients. Simple relations between them allow to determine triple and quadruple cluster operators which can be used in the standard CC equations for singles and doubles. The so-called CC equations for singles and doubles can only contain up to quadruple cluster operators so the information about higher excitations than quadruple enters the equations through triples and quadruples. The singles and doubles depend on triples and quadruples while the energy on singles and doubles. This hierarchical structure allows to enter an external information to the CC equations. For example, if the exact triple and quadruple clusters are available then the exact energy can be obtained from the CC equations for singles and doubles. Having triples and quadruples extracted from the CAS SCF calculation one can transfer the information about nondynamic correlation obtained within CAS SCF into the CC scheme. Other external sources of this information, more or less reliable, can also be considered. Approaches of this type have been called the externally corrected CC methods [48]. Slightly different scheme has been proposed by Hino, Kinoshita and Bartlett under the name of tailored CC method [49] but the general idea underlying the approach is quite similar.

One of the most reliable yet still inexpensive sources of information on nondynamic correlation is MR-CISD. Disadvantages of MR-CISD are relatively poor description of the dynamic part of correlation and the lack of size-extensivity. An externally corrected CC scheme in which MR-CISD is used as a source of some triple and quadruple cluster amplitudes has been called the reduced multi-reference CC method (RMR-CCSD) [50]. It has been shown that the method is capable of providing good description of bond breaking situations where the degree of quasi-degeneracy is changing significantly with the geometry. It is well known that most of the genuine MR-CC approaches have a problem with a smooth transition from, for example, single-reference to multi-reference cases and that is one the main advantages of RMR-CCSD.

The RMR-CCSD method consists of several step. The first one is perform MR-CISD calculation for the ground state with properly selected reference space. The next is to take the Hartree-Fock determinant Φ as a reference and express the MR-CISD wave function in

terms of excitation with respect to it

$$\Psi_{\text{MRCI}} = (1 + C_1 + C_2 + C'_3 + C'_4 + \dots)\Phi, \quad (1)$$

In addition to the single and double excitations, C_1 and C_2 , there are also some higher excitations present in the expansion. They represent single and double excitations with respect to other determinants from the reference space so only some of them appear in the MR-CISD wave function expressed in this way. This fact is indicated by adding prime to higher than double excitation operators in equation (1). From C'_3 and C'_4 the T'_3 and T'_4 clusters operators can be obtained using simple relations between CI coefficients and cluster amplitudes

$$C_1 = T_1, \quad (2)$$

$$C_2 = T_2 + (1/2)T_1^2, \quad (3)$$

$$C_3 = T_3 + T_1T_2 + (1/3!)T_1^3, \quad (4)$$

$$C_4 = T_4 + T_1T_3 + (1/2)T_2^2 + (1/2)T_1^2T_2 + (1/4!)T_1^4, \quad (5)$$

and so on. The next step is to plug these amplitudes into the CC equations for singles and doubles

$$\langle \Phi_1 | [H \exp(T_1 + T_2 + T'_3)]_c | \Phi \rangle = 0, \quad (6)$$

$$\langle \Phi_2 | [H \exp(T_1 + T_2 + T'_3 + T'_4)]_c | \Phi \rangle = 0, \quad (7)$$

where H is the Hamiltonian, Φ_1 and Φ_2 represent singly and doubly excited determinants, respectively, and $[\]_c$ means connected terms only. For simplicity a nonlinear contribution to equation (7) involving T'_3 is neglected in RMR-CCSD [50]. Now an iterative procedure allows determination of T_1 and T_2 from the equations and calculation of the correlation energy from the standard CC energy expression.

The RMR-CCSD scheme is a combination of MR-CISD and SR-CC in which the MR-CISD method is responsible for the nondynamic part of correlation while the SR-CC one takes care of reliable description of the dynamic part providing the reference space is properly selected in MR-CISD calculations. An alternative approach based on a similar strategy

emerges when we assume that the MR-CISD method requires only some improvement of the dynamic correlation description and the reduction of size-extensivity error. A disadvantage of the MR-CISD scheme is that the linear expansion is used for both nondynamic and dynamic correlation so the description of dynamic part does not benefit from the efficiency of the exponential ansatz. The idea is to improve the MR-CISD wave function by adding additional terms that mimic the CC expansion. Since the correction concerns the dynamic part of correlation the SR CC expansion can be used. In the MR-CISD wave function, equation (1), only some higher than double excitation operators are included. Relying on the cluster analysis, equations (2)-(3), which enable us determination of T_1 and T_2 from C_1 and C_2 , the remaining excitation operators can be constructed in the exponential fashion

$$\Psi_{MRCI+\Delta CC} = (1 + C_1 + C_2 + C'_3 + C'_4 + \dots + Qe^{T_1+T_2})\Phi, \quad (8)$$

where Q projects out of the MR-CISD space. Thus contributions that are not present in the MR-CCSD function are now represented in a CC manner, i.e. through products of lower excitation rank cluster operators. If this modification of the wave function is expected to introduce a relatively moderate change in the description of the state then a noniterative treatment is justified resulting in a CC corrections to the MR-CISD energy. Usually the energy expectation value expression is used to reach this point and first of all the correction evaluates changes of the energy caused by modification of the wave function introduced in the so-called equation for C_2 . In this way we obtain [51]

$$E = E_{MRCI} + \langle \Phi | C_2^\dagger H Q e^{T_1+T_2} | \Phi \rangle = E_{MRCI} + \Delta_{MRCI}^D, \quad (9)$$

if only the equation for C_2 is modified. The second term constitutes the MR-CISD energy correction. If the equation for C_1 is also changed according to equation (8) then we have [52, 53]

$$\Delta_{MRCI}^{SD} = \Delta_{MRCI}^D + \langle \Phi | C_1^\dagger H Q e^{T_1+T_2} | \Phi \rangle. \quad (10)$$

The corrections can be called the coupled cluster corrections (CCCs) to MR-CISD and can be seen as a noniterative version of the RMR-CCSD method. On the other hand they can be also considered as Davidson-type corrections.

The corrections have been tested in many calculations and proved their effectiveness.

Their performance is very similar to that of RMR-CCSD method. They behave in a way similar to the regular CC methods meaning that they can handle quite significant degree of quasi-degeneracy but when the degree is too high they break down completely. The later can happen when the reference space in MR-CISD calculations is not sufficiently large to describe properly the nondynamic correlation thus the basic assumption is not fulfilled. Let us discuss properties of CCC on one numerical example which is the simultaneous stretching of H-O bonds in H₂O. The DZ model for which FCI results are available is used [54]. The model is frequently employed to test the performance of different methods in presence of various degrees of quasi-degeneracy. Fig. 1. shows energies of CISD, CCSD, (2,2)MR-CISD, (2,2)RMR-CCSD, and (2,2)MR-CISD+CCC ($CCC = \Delta_{MRCI}^D$) relative to the FCI energy. (2,2) means that we have CAS with two active orbitals and two active electrons as a reference space. The results show that for 1 R_e we have typical SR situation thus the (2,2)MR-CISD result does not differ much from that of CISD. At the same time both RMR-CCSD and CCC are capable of reproducing the CCSD energy. The real advantage of RMR-CCSD and CCC over MR-CISD and CCSD is visible for 1.5 R_e and 2 R_e. Having good description of both types of correlation in approaches combining MR-CISD and SR-CC good accuracy results are obtained in quasi-degenerate situations. Especially for 2 R_e the improvement is quite spectacular where ~ 32 mH MR-CISD energy gap is reduced to ~ 3 mH. The important feature of the methods is that it allows to proceed smoothly from single-reference to multi-reference situations. It is well known that the genuine MR-CC methods have difficulties in describing different molecular geometries using one reference space. Moreover, contrary to the MR-CC schemes, the approaches presented above are state-selective and are not plagued with the intruder state problem.

The CI methods are not size-extensive and it would be interesting to know to what an extent the CCC correction can reduce the inextensivity error. That can be followed on calculation performed for a model being a slight modification of the well known H8 system [43]. The model consists of four H₂ molecules with the internuclear distance fix at 2 a.u. initially arranged in the regular octagonal geometry. Then all H₂ molecules are

being simultaneously moved apart and their distance from the initial position is used as a separation parameter. Calculation performed for 4H_2 includes FCI, CISD, CCSD, (2,2)MR-CISD and (2,2)MR-CISD+CCC. All the methods are exact for two-electron systems thus in the limit of full separation the energy given by a size-extensive method with respect FCI should be equal zero. Fig. 2 presents energies of the methods plotted against the separation parameter values. For small values of the separation parameter the ground state of 4H_2 is quasi-degenerate, the CCSD method does not perform well and there is a big difference between the CISD and (2,2)MR-CISD energies. The CC correction does a good job in reducing the MR-CISD energy error and giving a result very close to that of FCI. Then the degree of quasi-degeneracy rapidly decreases, the difference between CISD and MR-CISD becomes small and the CCSD method behaves like in typically single reference cases giving very good estimate of the exact energy. Already for the separation parameter value equal 3 a.u. the H_2 molecules can be considered well separated. It is seen that the only method that is fully size-extensive is CCSD reproducing the FCI energy. The CC corrected MR-CISD energy is not equal the FCI one but the difference given by MR-CISD is drastically reduced by the correction. Thus along with increasing the accuracy the CC correction is capable of reducing the inextensivity error of MR-CISD.

To summarize let us stress that in view of the fact that MR-CISD is one of few methods which are used in routine multi-reference calculations, the CC corrections, as a way of making MR-CISD more accurate and less size-inextensive seems very attractive. Finally it should be mentioned that some attempts have been made to use similar approaches in description of excited states [55, 56].

3. Multi-reference MBPT and CC approaches

As mentioned in the introduction the so-called genuine MR approaches are based on the effective Hamiltonian formulation. We have found convenient and instructive to introduce the effective Hamiltonian formalism through simple similarity transformations [16]. Having the functional space partitioned into the reference space M_0 spanned by a set of reference determinants $\{\Phi_\mu\}$, ($\mu = 1, \dots, m$) and its orthogonal complement $M_\perp$ with the projection

operators P_0 and Q , respectively, we can introduce a nilpotent operator $X \equiv QXP_0$ ($X^2 = 0$)

and use it to perform the following similarity transformation of the Hamiltonian

$$\tilde{H} = e^{-X} H e^X = (1 - X)H(1 + X). \quad (11)$$

Requiring X to satisfy

$$Q\tilde{H}P_0 = Q(1 - X)H(1 + X)P_0 = 0, \quad (12)$$

we have the complete eigenvalue problem of H divided into two subproblems since now all eigenvalues of H can be obtained by separate diagonalizations of two diagonal blocks of $\tilde{H}$, $P_0\tilde{H}P_0$ and $Q\tilde{H}Q$. Assuming that we are interested in a subset of $m(= \dim M_0)$ eigenvalues of H only it is enough to solve the $P_0\tilde{H}P_0$ eigenvalue problem. The first step is, however, to find X that satisfies equation (12).

The $P_0\tilde{H}P_0$ operator is called the effective Hamiltonian

$$H_{eff} = P_0\tilde{H}P_0 = P_0H(1 + X)P_0 \quad (13)$$

Action of H_{eff} is restricted to reference (model) space and its eigenvalues constitute a subset of the eigenvalues of H . Which eigenvalues are included in the subset depends on X . Equation (12) is satisfied by many different X since is quadratic in X . Different X fulfilling equation (12) provide different subsets of the H eigenvalues, thus the problem is to find such X that leads to a set of energies we are interested in. If that is difficult to achieve then we can have what is called the intruder state problem [57] or multiple solution problem [29].

The two-step procedure introduced by the effective Hamiltonian formalism permits for adequate treatment of both types of correlation effects. The X operator should be responsible for dynamic correlation while diagonalization of H_{eff} should provide the nondynamical correlation contribution. To obtain good quality results it is not necessary to fully satisfy equation (12) but, for example, to a certain order of some perturbation expansion. Similarly a truncation of the $M_\perp$ space to that spanned by determinants that are singly or doubly excited with respect to at least one reference function Φ_μ can be used to approximately satisfy equation (12). That would be equivalent to MR-CISD but this time formulated within the effective Hamiltonian framework that provides several eigenvalues at a time. Finally a

coupled cluster expansion can be used that proved so effective in describing dynamic correlation effects in SR cases. One can see that for approximate schemes it is important to have X that do not have to deal with nondynamic correlation effects.

To apply many-body techniques it is essential to have Fermi vacuum defined. Then all operators entering equation (12) and (13) can be expressed as many-body operators and an explicit form of the equations can be obtained. As discussed in the introduction basically two strategies can be followed. Having

$$XP_0 = \sum_{\mu=1}^m XP_{\mu}, \quad P_{\mu} = |\Phi_{\mu}\rangle\langle\Phi_{\mu}|, \quad (14)$$

one may see attractive to use Φ_{μ} as a Fermi vacuum to define excitation operators in XP_{μ} and have different Fermi vacua for different components of X . Thus in the X equation corresponding to Φ_{μ} that is obtained from equation (12)

$$QH(1+X) - XP_0H(1+X)P_{\mu} = 0, \quad (15)$$

the first term is similar to that in the SR case in each equation. The difference is that all XP_{μ} must excite outside the reference space. The second term, however, is quite complicated since it couples equations for different Φ_{μ} . Another characteristic feature of the approach is that XP_{μ} of the same excitation-rank generate different subspaces of $M_{\perp}$ for different μ .

The second possibility is to use one Fermi vacuum Φ for all reference determinants. Hence, first the reference functions must be obtained from the vacuum by a sequence of particle-hole creation operators D_{μ}

$$\Phi_{\mu} = D_{\mu}\Phi, \quad (16)$$

and then orthogonal space determinants are reached by applying X that now must consists of particle-hole annihilation operators to annihilate the reference state generated by D_{μ} and a sequence of particle-hole creation operators to give the orthogonal space contribution. Here excitations in X of the different particle-rank can lead to the same excited function. There are many possibilities for making choice for Φ and whether D_{μ} consists of particle only, hole only, or particle-hole creation operators depend on this choice and the reference space selection.

There are two kinds of perturbation expansion associated with the above choices for the Fermi vacuum. The first one is represented by MR perturbation expansion proposed by Hose and Kaldor [18]. The general rules for obtaining diagrammatic representation of the expansion have then been supplemented with an easier to follow order-by-order derivation [58]. The MR perturbation theory that is based on the single vacuum has been formulated by Brandow [17]. Here the core determinant is selected to be the vacuum and reference functions are obtained by creating a number of particles on valence levels in all possible ways. Reference spaces generated in this way are complete. Obviously, D_μ contains only valence particle creation operators. This kind of perturbation expansion is especially convenient for description of atomic and nuclear systems. Another version of the perturbation expansion is obtained when the Hartree-Fock determinant for a closed shell neutral system is selected to be the vacuum and the reference determinants are generated by D_μ through creation of k particles on unoccupied active orbital levels and l holes on occupied active ones. Such reference spaces are usually denoted by (k, l) . With properly selected active unoccupied and occupied orbital levels a convenient tool for direct determination of excitation energies is obtained. Such a reference space is not complete. The concept has been developed by Hague and Mukherjee [24] and Lindgren [25] mainly in the context of MR CC applications. Within the perturbation theory framework it has been possible to show a link between single-reference PT calculation of excitation energies and multi-reference PT one and justify some approximations and simplifications made there [59].

The main focus of the MR developments has been on the MR-CC methods. In this case the use of different vacua for different reference functions Φ_i leads to different cluster operators for different Φ_μ .

$$(1 + X)P_0 = \sum_{\mu=1}^m e^{T^\mu} P_\mu. \quad (17)$$

The CC ansatz has been proposed by Jeziorski and Monkhorst [22] and the method is known as the Hilbert-space or state-universal. As mentioned the simplicity of the expansion causes that the first term in equation (15) looks like that in the SR-CC equations but makes the second (renormalization) term that couples cluster operators defined with respect to different vacua complicated. The method has been implemented and used in some small size

calculations [60, 29, 61, 62]. Also an interesting variant of the method, the two-determinant CC approach has been proposed, by Balkova and Bartlett [63]. Several generalizations of the method to include incomplete model spaces have been considered with quite recent involving the so-called C-condition [64]. The HS-CC scheme has also state-specific versions like the Brillouin-Wigner MR-CC (B-W MRCC) [65] or state-specific MR-CC (SS-MRCC) [66]. However, the problem all HS-CC approaches face is that for different μ subspaces of $M_{\perp}$ generated T_{μ} of the same excitation rank are different. The importance of this fact for the quality of the results has been emphasized by Berkovic and Kaldor [62].

The Fock-space or valence-universal CC method has been developed for many years by atomic and nuclear physicists and quantum chemists. The concept of the core determinant as a Fermi vacuum seems quite natural especially for atoms and nuclei. There are two major problems with excitation operators from the reference space defined with respect to a single vacuum. Defined as a second-quantized operators they can contain particle-hole annihilation operators so if they are used as cluster operators in the exponent then contractions between them are possible. The normal-ordered form of the exponential expansion thus can be very complicated. To avoid that the normal-ordered form of exponential expansion has been introduced by Offermann, Ey and Kümmel [19] and in a very elegant way by Lindgren [20]

$$(1 + X)P_0 = \{e^S\}P_0, \quad (18)$$

where $\{ \}$ means that operators are in the normal order so contractions between them are not allowed. The second important concept is valence universal strategy of solving the CC equations which has been introduced by Mukherjee [21]. This concept has been crucial to solve the problem of redundant cluster operators. The problem is that many different cluster operators lead to the same excited determinant while acting on the same reference function Φ_{μ} so the number of equations given by the effective Hamiltonian scheme is not large enough to determine all of them. Valence universal strategy assumes that the additional equations are provided by problems with lower number of quasi-particles than the desired one and shows that the equations can be solved in a hierarchical way. For example, for the $(k, 0)$ problem (with core and k valence particles) one has to solve the $(0, 0)$ problem first, then $(1, 0)$, etc. up to the final $(k, 0)$ problem. In each of them cluster amplitudes from lower

sectors of the Fock-space appear as known parameters so only those corresponding to a given sector must be determined. It should be noticed, however, that the CC equations can also be solved without valence-universal strategy employed but through generating perturbative contributions of certain types to the wave operator given by equation (18) [26].

The use of $(k, 0)$ reference spaces is convenient for atomic calculations. Already the four-electron Beryllium atom can be considered as a system having quasi-degenerate ground state. Unfortunately it has been found that with iterative procedures based on Jacobi-type algorithms it is not possible to converge the CC equations. A closer look at the problem reveals that this can be associated with the presence of the so-called intruder state which energy is close to those which we intend to obtain by diagonalization of the effective Hamiltonian. Thus for many years the VU-CC calculation for Be was seen as a classical example of the intruder state problem that enable to obtain solutions within MR-CC schemes. It appears, however, that the CC equations can be solved when more efficient iterative techniques are employed. With the use of the Newton-Raphson scheme the convergence has been finally reached showing that the method is capable of providing high quality results [28]. The Newton-Raphson iterative algorithm for solving sets on nonlinear equations is, however, numerically demanding and depends much on the starting vector. A different approach that can provide an efficient way of solving the FS-CC equations can be found when the fact that FS-CC expansion, equation (18), due to valence strategy of solving the FS-CC equations, is linear in the unknown cluster operators $S^{(k,0)}$ in the $(k, 0)$, $k > 0$, sector of the Fock-space. That suggests that diagonalization techniques can also be used to solve the equations. A scheme that emerges from this idea can be considered as an implementation of the intermediate Hamiltonian technique to the FS-CC method. The idea standing behind the intermediate Hamiltonian formalism is to obtain a part of X , that can cause divergence, by diagonalization. Thus diagonalization of a slightly larger matrix than that of H_{eff} is assumed. The matrix represents the intermediate Hamiltonian and it has all eigenvalues of H_{eff} among its eigenvalues. Because of specific features of FS-CC the intermediate Hamiltonian version of FS-CC is especially simple and both cluster amplitudes and energies can be obtained exclusively by diagonalization of the intermediate Hamiltonian. Thus the

standard iterative schemes for solving the CC equations are not required at all. To arrive at the intermediate Hamiltonian formulation we use, as before, similarity transformations of H [16]. The transformation leading to H_{eff} , equation (12), is split into a sequence of two similarity transformations by dividing X into

$$X = Y + Z, \quad Z = P_I X P_0, \quad Y = (Q - P_I) X P_0, \quad (19)$$

where P_I is the projection on the intermediate space that is defined as a subspace of the orthogonal space reached by cluster operators corresponding to a given sector of the Fock space. Let it be the $(k, 0)$ sector. Then $M_I^{(k,0)}$ is a subspace that is reached by excitations given by $S^{(k,0)} P_{(k,0)}$. It follows that then $Y^{(k,0)}$ contains only cluster operators from lower sectors than the $(k, 0)$ one since due to valence universal strategy the expansion is linear in $S^{(k,0)}$ at the $(k, 0)$ level. From equation (12) we have

$$P \tilde{H} P = P(1 - Z)(1 - Y)H(1 + Y)(1 + Z)P, \quad (20)$$

where $P = P_0 + P_I$ projects on the reference and intermediate space. Having the standard FS-CC equations satisfied ($P_I \tilde{H} P_0 = 0$) all eigenvalues of $P \tilde{H} P$ can be obtained by separate diagonalizations of two diagonal blocks ($P_0 \tilde{H} P_0$ and $P_I \tilde{H} P_I$). The first one is the effective Hamiltonian so eigenvalues of H_{eff} are among them. It is easy to see that the eigenvalues of $P \tilde{H} P$ are also given by

$$P \tilde{\tilde{H}} P = P(1 - Y)H(1 + Y)P, \quad (21)$$

since both $P \tilde{H} P$ and $P \tilde{\tilde{H}} P$ are related through similarity transformation in P . Thus eigenvalues of H_{eff} are among those given by

$$H_I = P(1 - Y)H(1 + Y)P = PH(1 + Y)P, \quad (22)$$

where H_I stands for the intermediate Hamiltonian (IH). The intermediate Hamiltonian version of FS-CC method is completely equivalent to the effective Hamiltonian one but offers an efficient way of solving the CC equations. The IH FS-CC formulation allows us to replace the two step procedure in the standard FC-CC method with a one step procedure in which eigenvalues and eigenvectors (from which cluster amplitudes can be determined)

are obtained simultaneously. Each eigenvalue can be obtained separately if diagonalization allowing single-root calculation is used and in this sense the method can be considered state-specific. Effective diagonalization procurers for non-symmetric matrices [68] allow to overcome the convergence and intruder state problems. Also roots corresponding to alternative solutions of the effective Hamiltonian formulation can be accessed without any problem. All this has been shown in the IH FS-CC calculation for Be [69] and other atomic systems [70].

Another problem that can be conveniently solved with the use of FS-CC method is the calculation of excitation energies. More general quasi-complete (k, l) reference spaces are needed in this case, first of all the $(1, 1)$ one since most of low lying excited states are dominated by single excitations. For excitation energy calculation also other methods like the equation of motion CC (EOM CC) [71, 72] or CC linear response theory (CC LRT) [73] can be effectively employed. These methods are not, however, fully size-extensive since they use linear expansion to describe excited states so only the ground state is parametrized by the exponential one. The starting point in all these approaches is the SR-CC calculation for the ground state where the ground state function is $\exp(T)\Phi$ and Φ is the Hartree-Fock determinant. The equation can be written as

$$\bar{H}\Phi = E\Phi, \quad \bar{H} = e^{-T}He^T. \quad (23)$$

In other words we are looking for such a cluster operator T for which Φ is the right eigenfunction of the similarity transformed Hamiltonian $\bar{H}$ corresponding to the ground state energy. Again similarity transformation is convenient to explain why excited states energies can be obtained as eigenvalues of $\bar{H}$ in the space spanned by excited determinants only. This fact was not completely clear and the procedure of neglecting Φ in the excited state expansion was considered as an approximation. Indeed diagonalization of the matrix representation of $\bar{H}$ in such a space does not allow determination of excited state wave functions directly and some additional simple calculation is necessary to obtain them but from the point of view of similarity transformations Φ does not have to be included as long as energies of excited states are considered.

The EOM CCSD method (or equivalently CCSD LRT) can be expressed in the framework

of effective Hamiltonian to make a comparison with the FS-CC approach possible. The comparison shows presence of disconnected contributions to the EOM CC effective Hamiltonian of the fourth order of perturbation theory [74]. When two separated systems are considered then local excitations are not affected by them, so the method can be called size-intensive, but nonlocal charge transfer excitation are not properly described. Also a minimal dressing to the EOM-CC matrix (CEPA-type) has been proposed to eliminate disconnected contributions [75]. The scheme has been implemented quite recently and the proper behavior of charge transfer excitations shown [76].

The FS-CC method with the (k, l) reference space has been proposed by Haque and Mukherjee [24]. The intruder state problem can hurt calculations of this kind but again the intermediate Hamiltonian technique can be used to ease the problem [77, 78]. It must be emphasized, however, that more general (k, l) version of the FS-CC method differs from the $(k, 0)$ version in one important aspect. The (k, l) sectors cannot be considered as different sectors of the Fock-space since some of them describe systems with the same number of particles like, for example, $(0, 0)$, $(1, 1)$, $(2, 2)$, ... or $(0, 1)$, $(1, 2)$, $(2, 3)$, ..., thus the same problem can be approached many times. For example, the $(0, 1)$ calculation, along with principle ionization potentials, can provide shake-up ionization potentials as an alternative solutions which are a primary goal of the $(1, 2)$ calculation. To avoid that a sequence of similarity transformations can be introduced leading to elimination of excitations to the lower sectors in the valence universal hierarchy [79]. The most important is, however, the $(1, 1)$ problem that is, as discussed, separated from the $(0, 0)$ one by taking $\bar{H}$ so the deexcitation operators can be omitted in $S^{(1,1)}$. The IH formulation can be obtained in a way similar to the previous case but now the hierarchy of calculations required is $(0,0)$, $(1,0)$, $(0,1)$ and $(1,1)$. An explicit form of the IH FS-CC equations on the CCSD level of approximation can be found in Ref. [78]. The IH formulation reviles several interesting features of the FS-CC method. The first is that at the $(1,0)$ and $(0,1)$ levels the eigenvalues of H_{eff} do not depend on the choice of active orbital levels but the cluster operators that are needed at the $(1,1)$ level do. The eigenvalues corresponding to some particular state are the same regardless whether they appear in the principle solution of the FS-CCSD method or in the alternative

ones. That also concerns the $(1, 1)$ sector. Another interesting observation is that the IH matrix elements can contain disconnected contributions. Connectedness of terms entering the CC equations is usually used to prove size-extensivity of a specific CC scheme. It can be shown, however, that here the disconnected contributions to IH do not hurt size-extensivity but, quite the contrary, are necessary to maintain size-extensivity since they cancel out disconnected terms generated by diagonalization of the IH matrix [78].

The IH FS-CC method has been implemented on the CCSD level [78, 80] and then extended to include three-body clusters (CCSDT) [81]. Note that SDT, due to specific definition of excitation operators, means one-, two- and three-body contributions to $S^{(k,l)}$ at all levels under consideration. Numerous calculations have shown that the increase of accuracy depends on the truncation scheme for the cluster operator and on the choice of active orbital levels. An example of typical behavior is shown in Fig. 3 where several vertical excitation energies for the H_2O molecule are presented. They are obtained with the IH-FSCC method at the SD and SDT level of approximation employing two different reference spaces. Here (m, n) means that m lowest-lying unoccupied orbitals and n highest-lying occupied ones are selected as active. It can be seen that the inclusion of three-body cluster operators is important to increase the accuracy when relatively small reference space is used in the calculation but it is not so important when larger reference spaces are used. Also larger reference spaces usually provide better evaluation of excitation energies as observed for H_2O in Fig. 3. The quality of the IH FSCC results is similar or slightly better than that of EOM CC but the FS-CC method offers size-extensive description not only of the ground state but also of excited states. The necessary condition for size-extensivity is a proper behavior of excitation energies in the limit of full separation of a system into noninteracting subsystems. As mentioned for excitations that are localized on subsystems excitation energies given by both methods in the calculation for the supersystem are the same as those obtained separately for the subsystems. This property is frequently called size-intensivity. However, those excitations that are really affected by the separation are of the charge-transfer character. For them the excitation energy should be equal to the sum of ionization potential and electron affinity. Fig. 4 shows the behavior of two lowest charge transfer excitations during separation of

the BeH₂ system into Be and H₂. The chart presents the difference between the excitation energies calculated for BeH₂ and the sum of corresponding principal IPs and EAs obtained for Be and H₂. The difference is corrected due to long-range coulombic interaction between charged fragments and shown as a function of the separation distance. The chart shows the nonzero EOM-CCSD energy gaps while for FS-CCSD both differences are reduced to zero. That proves size-inextensivity of EOM-CC.

Some other approaches that also try to employ diagonalization to solve the FS-CC equations must be mentioned here. These are the so-called eigenvalue-independent partitioning technique that is used to derive an alternative form of the FS-CC equations [84] and very similar if not identical idea called the canonical form of the Bloch equation [85]. The similarity transformed EOM-CC method that is based on quite different derivation also leads to a very similar working equations [86]. Quite different implementation of the intermediate Hamiltonian technique to FS-CC has been proposed by Kaldor group [87].

4. Conclusion

In this paper we present some recent multi-reference MBPT and CC developments with the main focus on those initiated at the Quantum Theory Project (QTP) University of Florida in Gainesville. Two approaches to the problem of quasi-degenerate and open-shell systems that are, in our opinion, very promising and provide robust computational schemes are described in more detail. They have been discussed in a broader context in order to show the advantages they offer. On the special occasion of 50 Years of the Quantum Theory Project the author would like to thank for the hospitality he has always experienced during his several visit to the Rod Bartlett group at QTP, first as a post-doc (1988-1990) and then as a visiting professor (1992, 1994, 1995). The unique scientific atmosphere of QTP has been always very inspiring to him. Many thanks to Rod Bartlett for his optimism and deep believe that all problems we straggle with can be solved.

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Figure 1: Energies of CISD, CCSD, (2,2)MR-CISD, (2,2)RMR-CCSD and (2,2)MR-CISD+CCC relative to FCI energy obtained for the DZ model of simultaneous stretching of H-O bonds in H_2O molecule [54]. The plot is based on results from Ref. [51].

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Figure 2: Energies of CISD, CCSD, (2,2)MR-CISD and CC corrected (2,2)MR-CISD relative to FCI energy obtained for the 4H₂ model. The 4H₂ model describes separation of four H₂ molecules arranged initially into regular octogonal geometry into nonintracting H₂ molecules. The plot is based on results from Ref. [53].

Figure 3: Vertical excitations energies for H_2O obtained with FS-CCSD and FS-CCSDT using POLI [83] basis set. Results for two reference spaces, (3,3) and (6,3), are depicted where (m,n) means m lowest unoccupied orbital levels and n highest occupied orbital levels being active. The chart is based on results from Ref. [82].

Figure 4: Behavior of two lowest charge transfer excitations for BeH₂ as a function of the distance between Be and H₂. The plot is based on results from Ref. [78].