A short journey through state-specific multi-reference many body theories

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Abstract: *In many body theories a good state-specific (SS) method, starting with a multi-reference function, takes care of the non-dynamical correlation due to near-degeneracy, and targets a specific state of interest via a state-specific wave operator bringing in the dynamical correlation by a cluster expansion inducing excitation to the virtual functions. All such methods are generically called as state-specific multi-reference (SSMR) methods. The SSMR methods address the solution of specific states of interest one at a time and are thus free from the intruder state problem as long as the target state is well separated from the virtual one.*
Key Words: *Intruder state problem, Multi reference based approaches, State specific theories*

I. Introduction

The traditional multireference (MR) coupled-cluster (CC) methods based on the effective hamiltonian are often beset by the problem of intruder states, and are not suitable for studying potential energy surface (PES) involving real or avoided curve crossing.

I discuss below as to how the problem of intruder states creeps in many body formulation by considering a system with a fixed number of electrons, described by the function ψ_a, the electronic Hamiltonian H and the eigenvalue E_a satisfying the Schrödinger equation

$$H\psi_a = E_a\psi_a$$

Let us define a subspace which contains the dominant part of ψ_a as the model space. Then a reference function ψ_a^o can be defined in this subspace which is related to ψ_a through a suitable mapping operator Ω (commonly referred to as the wave operator) such that

$$\Omega\psi_a^o = \psi_a$$

If all the possible combinations of the model space functions, that is, all $\psi_a^o \ \forall a = 1,2,3,\dots,N$, and a single wave operator Ω is used to get the corresponding excited states, the above equation is valid for all N. If Q is the virtual space projector, the wave operator then obeys the Bloch equation, with some partitioning of H.

$$Q[\Omega, H_0]P = Q(V\Omega - \Omega PV\Omega)P$$

The underlying Rayleigh- Schrödinger form of the first order wave operator satisfies:

$$Q[\Omega^{(1)}, H_0]P = QVP$$

and the expression for the matrix element of $\Omega^{(1)}$ connecting one model determinant ϕ_a to a virtual χ_l is

$$\Omega_{la}^{(1)} = \frac{V_{la}}{(< \phi_a|H_0|\phi_a > -< \chi_l|H_0|\chi_l >)}$$

As long as the virtual functions χ_l remain energetically well-separated from the model functions ϕ_a, the solution for the amplitudes of Ω remains well-behaved.

The SSMR methods considers the solution of a definite state of interest, one at a time, and are therefore devoid of the intruder states, as long as the targeted state is energetically well separated from the virtual functions. The formulation of a state-specific MR (SSMR) approach, thus, seems to be the only way to reach the goals set for a successful many-body theory.

II. The Goal: State Specific Multi-Reference Methods

The first proposal of a cluster expansion Ansatz in this context was due to Silverstone and Sinanoglu [1] using a combination of multi-determinant functions. This was the first attempt to develop a state-specific (SS) theory with the combining coefficients of the reference determinants being not updated iteratively along with the cluster amplitudes. This strategy results in the *contracted* or *unrelaxed* version of the theory. Several choices of

such reference functions are possible, depending on the degree of sophistication demanded at the zeroth order description. The most common choices are (a) a CAS configuration interaction (CAS-CI) or the more elaborate CAS based multi-configuration self-consistent field, CAS-SCF, function, (b) a CI or an MC-SCF function based on a quasi-complete active space (QACS), (c) a strongly orthogonal generalized valence-bond (SO-GVB) function. Nevertheless there have been instances of using SR starting point descriptions with selective higher rank cluster operators to a SS approach [2,3,4,5]. There are SS methods that start with a truly MR function, that accounts for the non-dynamical correlation stemming out the quasi-degeneracy, and targets a specific state of interest via a suitable state-specific wave-operator that incorporates dynamical correlation through cluster expansion inducing excitation to the virtual functions [6,7,8,9,10,11].

Among the many variants of SSMR methods proposed in the literature, the methods of Malrieu and co-workers[12,13], Mukherjee and co-workers[6,10,11] and Hubač and co-workers [14,15] are based on the Jeziorski-Monkhorst Ansatz (JM) have been systematically studied both theoretically and in several applications. The development of Mukherjee and co-workers and Hubač and co-workers and further developed by Pittner *et al* [16] are both based on the full JM Ansatz [17], while Malrieu and co-workers use the low order quasi-linearized truncation schemes of the JM wave operator.

2.1 Comparison Between Different Variants of SSMR Methods

Using the theory of state-specific self-consistent intermediate Hamiltonians, Malrieu and co-workers prescribe a new dressing of a multireference (MR) singles and doubles configuration interaction (CI) Hamiltonian matrix which ensures size consistency. The method is based on a coupled cluster (CC) type factorization of the coefficients of the triples and quadruples and can be considered as leading to a dressed CI formulation of a state-specific MRCC method.

The multireference Brillouin-Wigner CC (MR BWCC) method proposed by Hubač and co-workers does not suffer from intruder states and has only a linear scaling with the number of references and very simple amplitude equations, however, due to presence of unlinked terms, it is no longer size extensive. The MR BWCC method with an approximate size-extensivity correction has been successfully applied to a variety of diatomics and also to larger, chemically interesting systems[18]. However, the a posteriori correction[19] is only approximate and this leaves a question about the reliability of the method. Moreover, the corrected amplitudes do not correspond to any converged amplitude equation, which precludes the application of the usual gradient techniques. The new MRCC approach proposed by Hanrath[20] does not seem to be computationally competitive yet.

The state-specific MRCC method proposed by Mukherjee *et al*. [6,10,11] has been developed into a powerful method for chemical research in several recent studies[21,22,23]. Evangelista *et al*.[21] has renamed SS-MRCC as Mk-MRCC (Mukherjee's MRCC theory). The first production-level program (PSIMRCC) for Mk-MRCCSD has been coded into the freely available PSI3 package. Moreover, a hierarchy of Mk-MRCCSDT-n (n = 1a, 1b, 2, 3) methods for the iterative inclusion of connected triple excitations has been formulated and implemented for the first time. It has been investigated by Evangelista *et al*.[21] who developed explicit formulas for the coupling terms present in this approach[22]. Recently, this method has been implemented by Evangelista *et al*.[23] at the singles, doubles, and iterative triples level and other iterative approximations thereof and an alternative formulation of its amplitude equations with simpler coupling terms has been developed by Pittner and co-workers *et al*. [24]. Comparing with experimental data Evangelista *et al*.[22,23] shows that the Mukherjee's SS-MRCC method (referred as MkMRCC) is generally superior to the Brillouin-Wigner (MRBWCC) theory in predicting energies, structures, and vibrational frequencies for various chemically interesting systems. In their papers, they have commented ``MkCCSDT theory-a multireference coupled cluster method that is size extensive, intruder free, and that can potentially achieve chemical accuracy-is a prominent target for future development". Moreover, when Evangelista *et al*. analyzed the effect of the truncation of the excitation level, we found that MkCC shows a faster convergence to the FCI limit than BWCC. We thus concluded that even at the singles and doubles level, MkCC may provide accurate potential energy curves and that the inclusion of full triples promises to deliver energetics accurate to better than 1 kcal.mol^{-1}.

Mk-MRCC method is manifestly size-extensive, orbital invariant and size-consistent. This formalism is not just a trivial application of the state-universal MRCC (SU-MRCC) [17] multi-root formalism to one root of interest. It is altogether a new formalism, with the working equations quite different from that of the SU-MRCC theory. Since the SS-MRPT theory uses the same Ansatz as in SU-MRCC, it has more degrees of freedom than is needed to generate one root. This flexibility, in fact, is an advantage and is exploited to achieve the twin desirable goals: (i) avoiding intruders, and (ii) generating an explicitly size-extensive formalism.

Recently Das *et al*.[25] propose an externally corrected size-extensive single-root multi-reference CC (ecsr-MRCC) formalism, which is intruder-free and simpler in structure as compared to the parent SS-MRCC theory.

In all these SSMR many-body methods, the diagonalization of the effective operator in the model space generates the energies associated with altered coefficients for the model space functions, and hence the methods generate relaxed coefficients for the model space functions. The real advantage of relaxed SSMR theories over the unrelaxed ones may be more clearly understood in consideration of the mixed states, e.g. those electronic states of different types as valence and Rydberg, or covalent and ionic, which contribute strongly to the wave function. The relative importance of different types of states tend to vary strongly with the variation in molecular geometry. In considerations of such states the difference in coefficients of reference wave function and that of the actual correlated function is appreciably large. Hence a computational model warranting relaxation of the model space coefficients in the correlated treatment provides a conceptually correct description of this mixing.

Adamowicz and co-workers [26] suggested a state-specific formulation where a special role is played by one reference determinant which is more dominant than the rest. The entire cluster expansion is performed with respect to this determinant. The specific choice of the exponential Ansatz by Adamowicz and co-workers lead to no redundancy problem of cluster amplitudes. Their fully exponential Ansatz avoids redundancy problem because it generates all the needed excitations from the single formal reference determinant, thus making a clear separation between the occupied and unoccupied, and between active and inactive orbitals. The non-dynamical correlation is brought into the formulation by including in the cluster operator three- and four-body terms with at least one active orbital different from those present in the dominant determinant. There is a closely related formulation by Stolarczyk [27]. Since all the cluster operators are defined with respect to a pivotal determinant, these formulations are not really based on an MRCC approach. Moreover, the presence of three- and four-body operators makes the organization of the equations rather complex. Very recently Ivanov and Adamowicz [28] proposed a new state-specific multi-reference CC method termed as CASCCSD where the CASSCF wave function is used as the reference. The spirit of the approach lies in the partitioning of the entire set of CAS orbitals into the active and nonactive ones followed by the construction of coupled cluster wave functions which involve the excitation into the orbitals of the different sets. The present SS-MRCC formulation on which we base our work does not warrant the presence of a dominant determinant in the reference function. In this sense, it is more general and involves fewer sets of terms/diagrams to achieve similar accuracy. The most elaborate scheme uses conditions where each cluster amplitude is scaled accordingly to the values of the corresponding Hamiltonian matrix elements. Truncations up to the single and doubles seems like an intuitively interesting choice, although a rigorous formulation for all ranks of cluster operators is rather difficult.

In the other state-specific development of Mahapatra *et al.* [9], different types of sufficiency conditions have been imposed, which follow from the assumption that the total energy E is a sum of dynamical E_d and non-dynamical E_{nd} correlation energies. There is pivotal function with respect to which the dynamical correlation is defined. The dynamical correlation energy stems from the virtual functions which are reached by cluster operators acting on the pivotal function. The cluster operators acting on the other reference determinants generate contributions to the non-dynamical correlation energies. Thus the sufficiency conditions in Ref. [9] are different from the recent SSMR formulations [10,11,29,30] which are evidently more straightforward compared to this SSMR theory[9].

The SS-MRCC theory of Mukherjee and co-workers shows a number of appealing features: (i) It is a genuine MRCC method that treats all references in the model space on an equal footing. (2) It is rigorously size extensive and leads to size-consistent energies when localized orbitals are used. (3) The theory is free from intruder states. (4) The resulting equations can be written in terms of the usual similarity-transformed Hamiltonian matrix elements plus off-diagonal coupling terms. The coupling terms refer to the ``same vacuum'' and thus are not difficult to implement. (5) The SS-MRCC method works in both CMS and IMS. (6) The method is an explicitly spin-free in nature. (7) Finally, applications to atoms, small molecules, and medium-size molecules using SS-MRCC truncated to singles and doubles as well as triples have validated the accuracy of the theory vis-à-vis experiment and other theoretical methods.

As a practical tool of being applicable to bigger molecules, a full-blown SS-MRCC (Mk-MRCC) developed by Mukherjee and co-workers would be rather demanding computationally. It is needless to say that the success of SS-MRCC (or Mk-MRCC) in dealing with intruders and maintaining manifest size-extensivity, and hence serving as a tool of immense potential to generate complete PES of molecular species with arbitrary complexity and generality has paved the path towards the development of physically motivated simplified versions of the full-blown method to deal with systems of real chemical interest in a computationally tractable manner. It thus seems that an effort should be spent at further development of physically motivated approximation schemes which capture a substantial portion of the correlation of the full-blown theory starting from the SS-MRCC and it various variant (such as perturbation and CEPA-like approximants which are computationally economical) method proposed by Mukherjee and co-workers. The SS-MRCC method of Mukherjee and co-workers allows transparent simplification via truncation of the working equations, leading to various perturbative methods (called by us as SS-MRPT[29,30,31]) and CEPA-like aproximants of practical utility

which are designed to capture the essential strength of the parent SS-MRCC method without significant sacrificing its accuracy.

Another approach for treating the quasi-degeneracy in an intruder free manner is adopted by the various MR-based CEPA methods, which have appeared parallely along with the SS-based MRCC and MRPT methods. The earlier developed state-specific MRCEPA methods[32,33,34,35,36,37,38] avoided the redundancy problem using non-redundant cluster operators to compute the dynamical correlation on the zeroth order MR wave function.

Mukherjee and co-workers have recently suggested a suite of CEPA-like approximants[39,40] to their earlier formulated SS-MRCC[6,10] formalism based on a CAS, which show promise in their numerical performance *vis-a-vis* the parent theory. These theories, generically called SS-MRCEPA [39,40], were much simpler than the SS-MRCC, yet they captured most of the essential physics; in particular they bypassed intruders naturally as in the case of the parent theory also had this property. They were all rigorously size-extensive.

III. Conclusion

Despite the success and elegance of CAS-based SSMR- based CC, PT (such as CASPT, MRMPPT, MCQDPT, SS-MRPT etc) and CEPA-like formalisms one objection is the exponential increase of the size of the model space when one increases the number of active orbitals. Among the CAS determinants, only a small percentage has a significant weight in the wave function, and a formalism based on a multireference non- CAS wave function seems highly desirable from a computational point of view. Although recently much more attention is being focused on the various developments and subsequent implementations of SSMR type methods, but the main criticism of the theories based on the wave operator of Jeziorski-Monkhorst type is its prohibitively increasing number of amplitudes, since the cluster operator is defined with respect to each reference determinant. In Jeziorski-Monkhorst (JM) Ansatz-based SSMR method, more parameters are needed to be optimized for treating a single state only and as a result of this, numerical implementation is not computationally cost effective. The criticism regarding the proliferation of cluster amplitudes in a theory using JM Ansatz is quite relevant. But this proliferation is shared by all such formalisms currently in use and not just confined to the Mk-MR (such SS-MRCC, SS-MRPT and SS-MRCEPA) formalism only. Thus it is worthwhile to develop a MR theory which efficiently avoids the problem of intruders and is simultaneously computationally economical. The number of cluster amplitudes of the method considered can be reduced using a contracted description of the Ansatz of the starting wave function as that of the contracted MRCI (Multireference Configuration Interaction) method such as positing the sensible approximation of equal amplitudes for all the one- and two-body inactive to virtual excitations. Since inactive excitations are numerous, such an assumption will lead to drastic reduction of the number of cluster amplitudes. This would amount to an `Anonymous Parentage for the Inactive excitations' (API). Very recently, Mukherjee and co-workers provided a version of SS-MRPT, termed as Anonymous Parentage for the Inactive excitations SS-MRPT (API-SSMRPT), which is very effective in drastically reducing the number of amplitudes without undue sacrifice in accuracy[41,42]. The API-SSMRPT approach will open a possibility towards an accurate treatment for the states of arbitrary quasidegeneracy of small to large molecular systems since there is a drastic reduction of the number of cluster amplitudes in this approximation.

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