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Ab initio method with general model space: A challenge For Electronic Structure Theory

Dola Pahari
Assistant Professor, Department of Chemistry, Maharaja Manindra Chandra College, 20, Ramkanto Bose Street, Calcutta 700 003, INDIA.
Corresponding Author: Dola Pahari

Abstract: *The main difficulty in any CAS-based MR method calculations arises from the use of CAS in constructing many-electron wave functions as the exponential increase of the size of the model space when one increases the number of active orbitals and electrons. Thus CAS often generates too many configurations, and the size of the active space can outgrow the capacity of the present technology. To alleviate this problem, many approaches have been proposed. One can use the incomplete model space(IMS) scheme to attenuate the computational cost.*

Key Words: *Intruder state problem, Incomplete model space, Complete model space, Intermediate normalization*

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I. Introduction

Multi-reference (MR) many-body approach is one of the most promising avenues to describe electron correlation in molecular states which have varying degrees of nondynamical correlation. Most such traditional formulations were all based on the effective Hamiltonian framework [1,2,3,4] defined in a complete model space (CMS) [also called, a complete active space (CAS)]. Both perturbative[1] and coupled cluster (CC) [2,3,4] formulations were developed and their rigorous size-extensivity were established. The model functions furnish the nondynamical correlation and the virtual functions bring in the dynamical correlation. In molecular applications, their practical use remains somewhat restricted to this date due to the notorious `intruder problem' [5], which stems from near-degeneracy of some virtual functions with some high-lying model functions. The problem of intruders can be avoided using *incomplete model space* (IMS) instead of CMS, where the offending model functions mixing strongly with the virtual functions are deliberately kept out of the model space. Generally, the reference functions that dominate the wave functions corresponding to the low-lying excited states span an incomplete model space, because in most chemically interesting systems, these low-lying excited states are likely to be associated with single and double excitations from the ground state instead of attributing a given number of active electrons and active orbitals to all possible excitations. If one shifts the high-lying functions of the CMS to the virtual space (thereby making the model space incomplete in nature), this seems like a natural starting point from the physical point of view, where one may avoid intruders and at the same time target the low-lying states of interest.

II. Incomplete Model Space

All the standard versions of MR theories with effective Hamiltonians exploit the use of CMS to maintain the connectedness of the effective Hamiltonian, which automatically ensures the extensivity of energies. Such, unfortunately, is not the case in an IMS-based theory. Even if it were possible to get a connected effective Hamiltonian in an IMS, the computed state energies on diagonalization would still have been inextensive, just as in a CI in an IMS. The theoretical constraints on the effective Hamiltonian, which would guarantee the size-extensivity of the energies, is obviously somewhat more intricate.

The reason for appearance of size-inextensivity in a diagonalization of even a connected operator in an IMS can be traced by looking at the diagonalization problem as an infinite order perturbation theory, thereby monitoring all the connected and disconnected terms that are generated at each order of perturbation. If one of the model functions is chosen as the unperturbed function for one of the target energies, and the other model functions are taken care of, in an IMS, interacting via the matrix elements of a connected operator by a Rayleigh- Schrödinger (RS) perturbation, then at each order there will be two kinds of terms: (i) the so-called direct term, which involves a sum over states involving transitions from the starting model function to all the other model functions, eventually returning to the starting model function itself, and (ii) the so-called normalization term, which involves a product of a norm correction involving the perturbation correction of the

wave function and energy shifts with various orders of perturbation, with a negative sign. The normalization term gives rise to two distinct types of entities. In one, there are no common orbitals among the norm factor and the energy shift factor. They are, therefore, algebraically disconnected, and size-inextensive. By adding certain sets of similar such terms together and by using what is known as the Franz-Mills identity[6] the disconnected terms can be written as a sum over states expression just like as in the direct term. The intermediate states entering the sum in this expression are generated by the same excitations from the unperturbed functions as are involved in each factor of the disconnected normalization term, but the intermediate states are produced by the action of these excitations on some other model function generated by these excitations, rather than on the starting unperturbed function itself. If these intermediate functions thus generated belong to the IMS, then they would be exactly cancelled at the same order of perturbation stemming from a direct disconnected term, which necessarily involves only the sum over the model functions in the IMS. If, on the other hand, an intermediate state generated does not belong to the IMS (this will always happen for some terms, when the model space is incomplete), then such disconnected normalization terms will never get canceled by the analogous disconnected counterterms from the direct term, simply because there is no such intermediate state in this term. This is the real reason behind the appearance of disconnected terms at each order of perturbation while following the diagonalization procedure in an IMS as an infinite order perturbation theory. It should be mentioned here that there is another set of normalization term where there are common orbitals in the two factors. These so-called EPV (exclusion principle violating) terms are thus algebraically connected and, hence are harmless as far as size-extensivity is concerned. Because in a CMS, excitation on any model function to another involves only active orbitals, they lead only to excitations involving the functions in the CMS itself, and hence, all the disconnected terms from the normalization term get cancelled by a corresponding direct term. In contrast, although the excitations from the starting model function to another model function in a perturbation still involves only active orbitals, the intermediate states generated come from the action of these excitations on model functions other than the starting one, and these may belong to the complementary active space which, together with the starting IMS, span the CMS. Because the intermediate states appearing in the direct term never involve the functions of the complementary active space, these disconnected normalization terms never get cancelled by any of the direct terms. This analysis holds as much for a diagonalization on a connected effective Hamiltonian in an IMS as for a CI in an IMS. Thus, if one could ensure that excitation from the starting model function could be confined to only those whose action on other model functions restrict the excitation also only within the IMS, then there would not have been any disconnected term in the perturbation involving intermediates lying outside the IMS, and the problem of inextensivity would go away for the perturbative diagonalization of the matrix of the connected operator in an IMS. Because one can start with any model function as the starting unperturbed function, it follows that it is necessary that the effective operator should be such that any excitation involving this operator should not lead to excitations outside the IMS by its action on any model function.

Following the earlier works of Mukherjee [7,8] excitations connecting the model functions are called as `closed□. In contrast, types of excitations where their action on some functions in the IMS generates functions in the IMS, but their action on some other model function takes them to the complementary active space, are called ``quasi-open".

The effective Hamiltonian should be both connected and ``closed" for ensuring extensivity of the target energies on diagonalization in an IMS. It was shown by Mukherjee [7,8] that this can be ensured by including in cluster operators in the wave-operator, Ω not only excitations leading to virtual functions (via excitations which we will call `open') but also all the quasi-open excitations. The latter involves excitations with only active orbitals but, in contrast to the closed operators, may or may not lead to excitations to the complementary active space. The cluster amplitudes for the quasi-open operators should be determined from the `decoupling conditions□ that the matrix elements of all the quasi-open components of the transformed operator $L = \Omega^{-1}H\,\Omega$ should vanish. This can be accomplished in a straightforward manner via the use of Bloch equation in an IMS. Mukherjee showed that, if one includes in Ω only open and quasi-open operators (which is the minimal decoupling conditions), then it can generally so happen that the customary intermediate normalization for Ω would have to be abandoned. Actually Mukherjee *et al.*[7,8] have stressed that intermediate normalization has to be abandoned for general incomplete model spaces in order to satisfy generalized extensivity, while keeping the JM parameterization of the wave function. This comes about because the quasi-open operators can lead to excitations within the IMS and also because products of quasi-open cluster operators can be closed as well. By including only open and quasi-open operators in Ω, extensive MRCC formalisms have been developed. Such formulations were developed in the Fock-space MR coupled cluster (MRCC) theory by Mukherjee [9,10] and elaborated further later [7,8,11,12]. Applications of the formalisms [13] could, however, bypass the intruder problem only at certain specific nuclear geometries. They were more suitable for computing spectroscopic energy differences. The size-extensive and size-consistent Hilbert space MRCC (SU-MRCC) theory based on IMS has been proposed by Mukherjee and co-workers [14] and independently by Meissner, Kucharski and Bartlett [15], and

both following work by Mukherjee *et al.*[7,8,11,12] for the Fock space approach in an incomplete model space. State-specific MRCC theory has been developed using the same idea.

The decoupling conditions implicit in the Bloch equation for an IMS impose vanishing amplitudes for all the open and quasi-open operators of the transformed Hamiltonian *L*. Clearly, this still leaves open the possibility of choosing the closed component of Ω, viz Ω_{cl}. The normalization that comes closest to the intermediate normalization for Ω would be to choose Ω_{cl} = 1cl. The more desirable choice PΩP= P would be incompatible with the decoupling conditions $L_{q\text{-}op}$= 0, because these conditions, rather than certain arbitrary conditions imposed on $\Omega_{q\text{-}op}$, determine $\Omega_{q\text{-}op}$.

Of course, it is desirable to look for a size-extensive method for IMS using IN for Ω, because, for one, this would generate a simpler expression for H_{eff} just as in a corresponding theory using CMS and, for other IN, allows a straightforward generation of the cluster amplitudes from a knowledge of the CI coefficients for an exact function. However, the situation is rather tricky. One may imagine that, once a size-extensive formalism is developed with a cluster ansatz for Ω containing open and quasi-open operators, it is possible to introduce at the final stage of the formalism to impose the IN on the wave operator via the transformation:

$\widetilde{\Omega} = \Omega[P\Omega P]^{-1}$

which generates a new effective Hamiltonian $\widetilde{H}_{eff}$, given by:

$$\widetilde{H}_{eff} = P\Omega P H_{eff} \Omega [P\Omega P]^{-1}$$

Being a similarity-transformed operator of the original H_{eff}, $\widetilde{H}_{eff}$ produces the same roots. Such an approach was indeed suggested long ago by Chaudhuri *et al.* [16] who also pointed out the attendant difficulties. Though this stratagem does produce size-extensive energies, despite the use of IN for the wave operator, it is a post facto restoration of IN after having generated a connected H_{eff} without the IN. A straightforward generation of the modified wave operator $\widetilde{\Omega}$ without the intermediary of the Ω is not theoretically possible.

2.1 Comparison Between VU-MRCC and SU-MRCC based IMS Theories

Mukherjee and co-workers[17] have developed a valence-universal multireference coupled cluster (VU-MRCC) theory that can handle completely general incomplete model spaces, remaining close to the intermediate normalization, IN, condition for Ω as much as possible without violating extensivity and without the use of a post facto correction. In this formalism, the connectedness of the cluster operators as well as effective Hamiltonian and hence the extensivity of the corresponding roots is achieved by invoking appropriate decoupling conditions on the special type of wave operator $\Omega = \{\exp(S + X_{cl})\}$ satisfying the Bloch equations in the Fock-space S in an excitation operator and X is a closed operator (denoted by cl).

Mukherjee and co-workers have demonstrated in their paper[18] that though the effective hamiltonian is disconnected, it is nevertheless equivalent via a similarity transformation to a connected closed effective hamiltonian, implying size-extensivity of the computed energies. In this paper, they have taken a fresh look into the aspects of size extensivity using the VU-MRCC using IMS. They introduced a novel cluster operator representation Ansatz for a new wave-operator $\widetilde{\Omega} = \exp(\tilde{S})$ where $\widetilde{\Omega}$ excludes all intermediate powers of $\tilde{S}$ in any monomial generated by expansion of S, which are closed, even as a factor of an otherwise external operator. They then prove that the hierarchical decoupling as is valid for the VU-MRCC for CMS, the size-consistency of the associated $\widetilde{H}_{eff}$ via its equivalence to a connected H_{eff} as well as the simplicity of the algebraic expression of $\widetilde{H}_{eff}$ can be simultaneously satisfied. There is no need for the use of X_{cl} type of operator at all, in their formulation. It has not escaped their notice that a very similar idea can be invoked to generate rather simple working equations for the SUMRCC and the SS-MRCC as well.

Li and Paldus [19] have presented a new version of the state-universal multireference coupled-cluster (SU-MRCC) theory that is capable of handling completely general, incomplete model spaces. This is achieved by exploiting the concept of `locality' for the active molecular spin orbitals and by introducing the constraining conditions (C conditions) on cluster amplitudes that are associated with the internal excitations transforming one reference configuration into another one. These C conditions make it possible to represent the exact (i.e., full configuration interaction) wave function via the SU-MRCC cluster ansatz based on an arbitrary model space. The C conditions are then taken into account together with the standard SU-MRCC equations for the external amplitudes, thus enabling one to reach the exact result in the limit, while preserving the connectivity property and thus the size-extensivity. In their approach, the definition of the cluster operator is extended such that the wave operator satisfies intermediate normalization. This means that there may be elements in the cluster operator that excite between model space determinants and their coefficients exactly negate the product of disconnected excitation operators, each of which typically excite out of the model space. A simple example would be provided by the two dimensional model space $|a\bar{a}>$ and $|b\bar{b}>$. The single excitations with coefficients t_a^b and $t_{\bar{a}}^{\bar{b}}$ excite out of the model space when acting on $|a\bar{a}>$, but their product leads precisely to the second model space determinant. To impose intermediate normalization, Li and Paldus include the

additional cluster operator that excites between the model space determinants with coefficient $t_{a\bar{a}}^{b\bar{b}} = -t_a^b t_{\bar{a}}^{\bar{b}}$. In this way they maintain intermediate normalization, but the cluster operator contains manifestly disconnected parts. Li and Paldus refer to this definition of the cluster amplitudes that can excite within the model space as satisfying the C condition□. For large model spaces this prescription may require extending the cluster operator with potentially high rank excitation operators in order to satisfy this C condition, or, equivalently, intermediate normalization, which can make the implementation of the general scheme rather cumbersome.

There is another scheme on the theme of general model space SU-MRCC. In this approch, the cluster operators do not contain any excitations within the model space. This generally implies that for the incomplete model space intermediate normalization does not hold [17]. Irrespective of the additive separability or even connectivity of the effective Hamiltonian and cluster operators in the Li Paldus theory, the effective Hamiltonian may contain extensivity-violating components that are not explicitly equated to zero, and we anticipate that the energies obtained by diagonalizing the effective Hamiltonian will not satisfy generalized extensivity. The property of generalized extensivity is more amenable to diagrammatic analysis and requires operators to be connected [20].

The Hilbert space method is more appealing as to computing potential energy surface (PES) of several strongly interacting states over a wide range of geometries, For PES, there are usually different intruders in the different regions of the surfaces, and this precludes the use of a specific IMS which is free of intruders at all the interesting regions of nuclear geometry. This aspect promoted us to develop intruder free IMS-based MR method. The method of intermediate Hamiltonians (IH) [21] tries to bypass intruders by abandoning the requirement that the roots strongly affected by intruders in the diagonalization of an effective operator are eigenvalues of H. A problem with IH method lies in having rigorously size-extensive formulations, though there have been two such attempts in the Fock-space context [22,23].

2.2 SS-MRCC Based IMS Theory

An attractive alternative is to develop state-specific (SS) MR many-body formalisms. So long as the state-energy remains energetically well-separated from the virtual functions, the intruder problem would be tackled in a much better manner. This method does not suffer from intruder states and size-extensive due to absence of unlinked terms. The SS-MRCC (or Mk-MRCC)[24] formalism is not just a trivial application of the SU-MRCC[4] 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.

Mukherjee and coworkers have developed a SS-MRCC based IMS formalism. The new formulation of the IMS based SS-MRCC theory is rigorous in the above-defined sense. The standard version of this theory requires a CMS if the connected character and thus size-extensivity is to be warranted. This is certainly a highly demanding and impractical requirement. In most instances of chemical interest, the low lying excited states are likely to be associated with single and double excitations from the ground state rather than with all possible excitations associated with a given number of electrons and active orbitals. Indeed, the configurations that dominate the wave functions of a few low-lying excited states form in general an IMS. Despite the success of the SS-MRCC[24], or its perturbative[25] and CEPA-like[26] variants, they are rather computation-intensive, since they work with a CMS. The choice of a CMS in a state-specific formalism is mainly dictated by the desire to achieve size-extensivity. An attractive alternative to a CMS-based formulation is to use some IMS which lead to proper fragmentation for some limited fragmentation channels. One such IMS is the quasi-complete model space (QCMS), used in many-body formalisms [7,8,9,11,12,27] based on the effective hamiltonians. Perturbative formulations using QCMS in the state-specific perturbative context was first developed by Nakano, Hirao and other co-workers [28,29].

Starting from an arbitrary IMS, a rigorous state-specific many-body method theory must preserve the size extensivity and at the same time be exact in the limit in which all clusters are taken into account in this chapter. If one simply applies the CMS formalism to an IMS, disconnected terms appear, since in this case a product of ``external'' excitations can produce an ``internal'' one. When such disconnected terms are simply neglected, the resulting method cannot be exact [i.e., cannot recover the full CI (FCI) result] even when all the clusters are accounted for. The IMS SS-MRCC method, of course, requires for its actual implementation in studying fragmentation processes a rather appropriate IMS, and the most suitable such IMS is the QCMS. Perturbative and CEPA-like schemes can be derived from the formalism in a straightforward manner.

The development of SSMR based IMS theory may also have useful potential to avoid or at least to attenuate the instability of the theory when the virtual determinants do not remain reasonably well-separated in energy from the state energy. The size-extensivity of the formalism will automatically imply the size-consistency of the computed energies, if the IMS is product- separable into the IMS for the various fragments. The theoretical constraints required for effective Hamiltonian (of SSMR formalism) to ensure size-extensivity of the energies in an IMS is more subtle and requires a careful analysis of the essential reasons behind the lack of size-extensivity of eigenvalues of even a connected operator in a matrix space which is IMS. The size-extensive formulation in the IMS warrants abandoning the intermediate normalization convention for the wave operator.

III. Conclusion

The major difference between the CMS and IMS (general model space, GMS)-based theories stems from the fact that in the latter case the products of lower-order external excitations can produce higher-order internal excitations, which in turn lead to disconnected terms in both the effective Hamiltonian and the coupling coefficients. If these disconnected terms are dropped, the consistency of the SS-MRCC equations is violated and the resulting theory cannot produce the exact result in the limit when all clusters are accounted for. Following the earlier analysis of Mukherjee that, in general, the use of the intermediate normalization for wave operator is incompatible with the size-extensivity of the target state energy computed via SS-MRCC theory. In the context of the SS-MRCC IMS the concept of the quasi-open and closed operators have been used, tracing the origin of the size-inextensivity of the computed energies to the appearance of the quasi-open matrix elements of H in a CI with IMS. It has been emphasized that the size-extensivity of the energies is predicated by the use of a connected effective Hamiltonian which is closed.

The intermediate normalization convention of the wave operator has to be abandoned in favour of some appropriate size-extensive normalization. Suitable operators, defined in Fock space described as closed, open and quasi-open have to be introduced to ensure that the effective operator furnishing the target energy on diagonalization is a closed operator.

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