Perspectives of APSG-based multireference perturbation theories

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Abstract

Applicability of antisymmetrized product of strongly orthogonal geminals (APSG) type wave functions, serving reference states for multi-reference many-body perturbation theories, is discussed. Emerging recent interest in this field indicates a promising future of this approach.

INTRODUCTION

Antisymmetrized product of strongly orthogonal geminals (APSG) represents a class of wave functions which contain a good amount of static correlation. It describes intra-pair correlation in the separated pair approximation exactly, but needs improvement to account for inter-pair dynamical correlation. A natural way of improvement is offered by perturbation theory (PT), which should be formulated as one of the various proposed versions of multi reference PT (MRPT). This paper shortly summarizes a few general features of MRPT, and discusses why APSG offers an appropriate reference state. We focus on a few selected recent papers published in this subject, and try to envisage what questions are to be addressed further.

SRPT VERSUS MRPT

Rayleigh-Schrödinger (RS) PT is a straightforward issue if one has a well defined Hermitean zero order Hamiltonian and its full spectrum is available. This condition is satisfied by single reference (SR) perturbation theory in the Møller-Plesset (MP) partitioning, where the zero order Hamiltonian is the N-electron Fockian, having Slater determinants as eigenvectors and the corresponding sums of orbital energies as eigenvalues. Such simple picture is not given in the multi-reference case. Essential differences between single- and multi-reference PT are collected in Table I. Various formulations of multi-reference PT differ in the way the problems listed in Table I are managed.

In our laboratory, two quite different MR formulations have been applied, starting from APSG as a reference.

The approach used in [1] and [2] focuses on the two-body nature of the zero order Hamiltonian having multi-determinantal eigenvectors. This follows the original idea by Dyall[3], and was recently elaborated and applied by Li[4] with success. These methods are designed for the specific structure of the zero order Hamiltonians and wave functions. They can be very effective in a given problem, but cannot be formulated to treat general reference states. In this respect the so called multi-configuration perturbation theory (MCPT), the second type of MRPT we investigated[5, 6], represents another extreme. It was formulated to be as general as possible, being capable of perturbing reference states of an arbitrary structure.

TABLE I: *Comparison of characteristics of SR and MR PT formulations.*

The zero order Hamiltonian is denoted by H^0, Φ_i^0 *and* E_i^0 *are its eigenvectors and eigenvalues, respectively. The perturbation is referred to by* W, Q *stands for the reduced resolvent. The reference state is* Φ_0^0, $P = 1 - |\Phi_0^0\rangle\langle\Phi_0^0|$ *is the projector orthogonal to the reference state. Abbreviation 'IC' means 'internally contracted'.*

<table>
<tr><th>SR</th><th>MR</th></tr>
<tr><td>$H^0 = \sum_i \varepsilon_i \; a_i^+ a_i$
– a natural choice for H^0
$H^0\Phi_i^0 = E_i^0\Phi_i^0$
The full set of 0th order functions is known
H^0 is one-body</td><td>H^0:
There is no natural choice
$H^0\Phi_0^0 = E_0^0\Phi_0^0$
Only a single MR wave function may be available
can be two-body</td></tr>
<tr><td colspan="2">$E^{(1)} = \langle W\rangle, \qquad E^{(2)} = \langle WQW\rangle, \qquad E^{(3)} = \langle WQ(W - \langle W\rangle)QW\rangle$
common formulae, but</td></tr>
<tr><td>Q is diagonal
$Q = \sum_{i\neq 0} \frac{|\Phi_i^0\rangle\langle\Phi_i^0|}{E_i^0 - E_0^0}$</td><td>$Q$ is not necessarily diagonal
$Q = \left(E_0^0 - PH^0\right)^{-1} P$</td></tr>
<tr><td>$\Psi^{(1)} = -QW|\Phi_0^0\rangle$
$= \sum_{i\neq 0} \frac{W_{i0}}{E_i^0 - E_0^0}|\Phi_i^0\rangle$
expansion in terms of zero order states</td><td>$\Psi^{[1]} = \sum_i d_i\Phi_i$
e.g. $\Phi_i = a_\mu^+ a_\nu|\Phi_0^0\rangle$, IC
expansion in terms of auxiliary functions</td></tr>
<tr><td>$\{\Phi_i^0\}$ are orthonormal</td><td>$\{\Phi_i\}$ can be overlapping</td></tr>
</table>

In the following these two possibilities of APSG based PT are summarized briefly, after a short outline of APSG itself.

THE ESSENCE OF APSG AND APSG BASED PT

The choice of an appropriate reference state is an important, problem-dependent issue in PT. As a guideline for its selection, Pople's conditions apply: it is preferably a variational upper bound, size consistent/extensive, exact for a two-electron system, and easy-to-construct. A complete active space (CAS) type wave function meets these criteria until the number of active electrons and active orbitals is small. The APSG function, which can be interpreted as a direct product of two-electron CAS functions, also meets the above criteria. It has the structure

$$\Phi_0^0 \;=\; \psi_{0,1}^\dagger \psi_{0,2}^\dagger \dots \psi_{0,N/2}^\dagger \;|\mathrm{vac}\rangle$$

where the two-electron geminal creation operators are expanded as

$$\psi_{0,i}^\dagger \;=\; \sum_{\mu}^{(i)} C_{\mu 0}^i \; \chi_{\mu\alpha}^\dagger \chi_{\mu\beta}^\dagger \qquad (1)$$

with both coefficients $C_{\mu 0}^i$ and natural orbitals χ_μ being optimized variationally. Label (i) on the summation indicates that natural orbitals are uniquely and exclusively distributed among geminals, a feature which ensures strong orthogonality of the wave function[7]. Index 0 refers to the ground state of geminal i.

At this point it is apparent that APSG represents a kind of intermediate between a complete and an incomplete model space. It is "complete" for each two-electron subunit (geminal), but lacks configurations originating from excitations from one geminal to another.

APSG-specific PT

The fact that orbitals are assigned to geminals in APSG offers a categorization of many-electron functions. Thinking in terms of intra- and inter-geminal excitations is particularly suited for constructing corrections to APSG, e.g. by PT.

Functions generated solely by intra-geminal excitations can be expressed via

$$\Phi_{i_1,\dots,i_{N/2}} \;=\; \psi_{i_1,1}^\dagger \psi_{i_2,2}^\dagger \dots \psi_{i_{N/2},N/2}^\dagger \;|\mathrm{vac}\rangle \;,$$

where at least one of the geminal state-indices $i_1, \dots, i_{N/2}$ differs from 0. Geminals arise as the solution of the local Schrödinger-equation, e.g. for geminal j

$$H_j^{\mathrm{eff}} \;\psi_{i,j} \;=\; E_{i,j} \;\psi_{i,j} \;, \qquad (2)$$

with

$$H_j{}^{\mathrm{eff}} = \sum_{\mu,\nu}^{(j)} \sum_{\sigma\in\{\alpha,\beta\}} h_{\mu\nu}^{\mathrm{eff}} \chi_{\mu\sigma}^+ \chi_{\nu\sigma}^- + \frac{1}{2} \sum_{\mu,\nu,\kappa,\lambda}^{(j)} \sum_{\sigma,\sigma'\in\{\alpha,\beta\}} [\mu\nu|\kappa\lambda] \chi_{\mu\sigma}^+ \chi_{\nu\sigma'}^+ \chi_{\lambda\sigma'}^- \chi_{\kappa\sigma}^- \;,$$

where the effective core $\mathbf{h}^{\mathrm{eff}}$ is responsible for inter-geminal Coulomb-repulsion and exchange interaction. Together with strong-orthogonality, the eigenvalue equation Eq.(2) ensures orthogonality of many-electron functions $\{\Phi_{i_1,\dots,i_{N/2}}\}$, including Φ_0^0 itself.

When wishing to incorporate inter-geminal excitations, the number of electrons assigned to certain geminal subspaces becomes different from two. For example, a single electron transfer from geminal j to k can be described via the functions

$$\Phi^{j:1,k:3}_{i_1,\ldots,i_{N/2}} = \psi^{\dagger}_{i_1,1} \ldots \psi^{\dagger}_{i_j,j}(1) \ldots \psi^{\dagger}_{i_k,k}(3) \ldots \psi^{\dagger}_{i_{N/2},N/2} \left|\text{vac}\right\rangle .$$

In subspaces j and k we do not have geminals in the strict sense: $\psi^{\dagger}_{i_j,j}(1)$ is a one-electron function, in return $\psi^{\dagger}_{i_k,k}(3)$ is a three-electron function. Still, both can be obtained as an eigenfunction to the respective effective Hamiltonian, $\hat{H}^{\text{eff}}_j$ and $\hat{H}^{\text{eff}}_k$. In principle, the procedure can be extended for any number of electrons transferred between any geminal subspaces. It has to be admitted however, that the cost of computing $\psi^{\dagger}_{i,j}(n)$ increases exponentially with the number of electrons n.

In terms of the functions described one can devise a MRPT for APSG, free from the difficulties collected in Table I. In particular the sum of geminal Hamiltonians

$$H^0 = \sum_{j=1}^{N/2} \hat{H}^{\text{eff}}_j \tag{3}$$

is a natural choice for a zero-order with APSG, which includes intra-geminal two-electron terms. The full set of eigenvectors to H^0 is provided by functions of the type $\{\Phi_{i_1,\ldots,i_{N/2}}\}$, $\{\Phi^{j:1,k:3}_{i_1,\ldots,i_{N/2}}\}$, etc. These functions are orthonormal and lead to a diagonal representation of the reduced resolvent.

Use of the zero order of Eq.(3) was first advocated by Kapuy[8, 9]. Constructing corrections in terms of geminal excitations have been explored by several studies since then, including those of Rassolov and coworkers[10], Li and coworkers[4, 11] and our group[1, 2]. It has been recognized that simultaneous intra-geminal (i.e. dispersive) excitations lead to divergence in PT when dissociating multiple bonds[1]. Recently a CEPA-0 type treatment has been reported, curing the divergent behavior[2]. Alternative PT methods have also been developed specifically for APSG, see e.g. Refs.[12–14].

A general PT framework applied to APSG

If not making recourse to the special structure of APSG, one can rely on the framework termed MCPT to devise a correction. The central quantity of MCPT is a non-hermitean zero-order Hamiltonian expressed in spectral form, via its eigenvectors and eigenvalues.

Right eigenvectors to H^0 are provided by the reference function, i.e. APSG and excited determinants. (Depending on the actual formulation, excited determinants may or may not be Schmidt-orthogonalized to APSG.) Right eigenvectors are overlapping, for this reason its reciprocal set is used as left eigenvectors of H^0. Construction of the reciprocal set necessitates the inversion of the overlap matrix. Due to the special choice for the right hand vectors, the inverse overlap can be expressed in closed form. Consequently, an analytic form can be given for the reciprocal vectors. Specification of the eigenvalues E_K completes the definition of the zero-order, fixing the partitioning.

The expression for H^0 eventually reads

$$H^0_{\mathrm{pMCPT}} \;=\; E_0|\Phi^0_0\rangle\langle\Phi^0_0| \;+\; \sum_{K\neq 0} E_K|K'\rangle\langle\tilde{K}'| \tag{4}$$

in the variant termed pMCPT, and

$$H^0_{\mathrm{uMCPT}} \;=\; E_0|\Phi^0_0\rangle\langle\tilde{\Phi}^0_0| \;+\; \sum_{K\neq 0} E_K|K\rangle\langle\tilde{K}| \tag{5}$$

gives the zero-order for the variant called uMCPT[15]. Summation over K excludes one determinant ($K = 0$) in both forms, to avoid redundancy. Usually the determinant with the largest coefficient squared in APSG is picked as pivotal, denoted $|0\rangle$. Writing the expansion of the APSG wavefunction over determinants as

$$|\Phi^0_0\rangle \;=\; \sum_K c_K|K\rangle \ ,$$

the primed and tilded quantities can be expressed as[6]

$$\begin{aligned}
|K'\rangle \;&=\; |K\rangle - c_K|\Phi^0_0\rangle \\
\langle\tilde{K}'| \;&=\; \langle\tilde{K}| \;=\; \langle K| \;-\; (c_K/c_0)\langle 0| \\
\langle\tilde{\Phi}^0_0| \;&=\; (1/c_0)\langle 0|
\end{aligned}$$

Various choices have been put forward for the zero-order eigenvalues, E_K[15]. A generalized MP partitioning has also been tested, operating with the single-reference Fockian based on the pivotal determinant[16–18]. Recently MCPT has got applied in the natural orbital functional framework also[19].

In view of Table I, there is indeed just one physically relevant zero-order MR function utilized in the MCPT framework. Excited zero-order functions emerge from a mathematical construction, in an extremely simple manner. The overlap of zero-order functions is handled by a bi-orthogonal formalism. As a consequence, expressions of bi-orthogonal RS PT[20–22] are to be applied in MCPT, instead of the common formulae cited in Table I. The zero-order of Eqs.(4) and (5) are formulated with Hilbert-space projectors, hence question of one- or two-body nature does not apply. The generalized MP variant[16] is different in this respect: it relies on a one-body Hamiltonian.

FEATURES OF MRPT

Both approaches detailed above are specimens of ”single-but-multi” techniques, targeting a single state. It is appropriate to mention here a class of MRPT, targeting multiple states at a time, to which Table I does not refer. These are the so-called perturb-then-diagonalize[23, 24] methods, sometimes called quasi-degenerate PT[25]. They typically rely on the Bloch-equation[26] or Van Vleck's PT formulation[27] to construct an effective Hamiltonian.

Selection of a model space is a delicate question in any of the MRPT methods. As a rule, all functions which become essential at some point of the potential surface studied are to be present in the model space. A valence CAS often includes more components than necessary, it however appears as the simplest choice, free from hands on control. The downside of a CAS reference is its unfavorable scaling with the number of active orbitals and electrons. It may also enhance intruder states, especially with effective Hamiltonian strategies. As a reference state for MRPT, the APSG wavefunction represents a fortunate balance between conflicting requirements, making APSG based MR treatments appealing for future exploration.

When discussing MRPT, one of the important properties to check is extensivity. Extensivity follows in a straightforward manner, whenever a theory is formulated in terms of diagrams. This holds for neither of the above discussed APSG-based methods. It is however possible to check size-consistency, i.e. additivity of the energy over non-interacting subsystems. Numerical tests indicate that MCPT is consistency-violating[5], similarly to related single-but-multi methods[28]. It is only the second order of uMCPT, with zero-order energies composed of one-particle quantities, which proves to be size-consistent[6]. In fact, several of the single-but-multi methods are consistency violating, with rare counter-examples[29]. In view of this, it is notable that the APSG specific PT, outlined above does have the potential of being size-consistent. Size-consistency of this approach follows in a trivial manner if zero-order functions are eigenfunctions of H^0 of Eq.(3), which is additively separable for non-interacting susbsystems.

Intruder states, i.e. quasi-degeneracy of the reference function with a perturbing function, is another important issue in connection with MRPT. The intruder problem of the PT specific for APSG has been mentioned already. Concerning MCPT, the question of intruders is closely related to the choice of E_K or the expression of the Fockian in the generalized MP partitioning. The best numerical experience has been obtained by the application of generalized ionization potentials and electron affinities as orbital energies[30], following the suggestion of Zaitevskii and Malrieu[31]. Such an idea was also successfully applied in the SR formulation[32].

Appearance of a pivotal determinant in MCPT has an unfortunate consequence: PT corrections are not invariant to the choice for the pivot. This drawback is shared with the more sophisticated MRCC method[33] which works over an active space but does not use any zero order reference. Pivot dependence is more expressed in uMCPT than in pMCPT. An averaging procedure has been suggested as a cure, which however enhances intruder-sensitivity[34].

The fact, that the APSG wavefunction is invariant to orbital rotations within geminal subspaces raises the question with any PT correction whether this property is preserved. Due to its generally applicable nature, the MCPT framework is obviously lacking in this respect. The PT method devised specifically for APSG has the potential of being orbital invariant. To reach this goal, one has to rely on the orbital invariance of geminal creation/annihilation operators. For corrections formulated solely in terms of geminal operators, e.g. Ref.[2], orbital invariance holds.

OPEN QUESTIONS OF APSG AND APSG BASED PT

As mentioned above, the reference state of Eq.(1) is a variational and extensive zero order state. Extensivity is meant here for processes dissociating two-electron subunits (cf. the He...He dissociation). It is also size-consistent if a process of single-bond dissociation is considered, as a consequence of treating two-electron subunits exactly. The APSG function represents an incomplete model space function, capable of capturing static correlation. These characteristics make APSG an ideal reference for MR based correlation treatment.

Some open problems associated with the APSG wave function are as follow.

(i) The singlet-coupled form of APSG, according to Eq.(1) is not capable to describe the correct spin-state of the fragments, if non-isolated bonds are involved in a dissociation process (i.e. a multiple bond or single bonds connected to the same atom). The problem has been solved by Rassolov via unrestricted orbitals and spin-adaptation[35]. The procedure conserves the variational and size-consistent character of the geminal wavefunction. No correlation corrections based on the wavefunction of Ref.[36] have been reported yet, though these would undoubtedly be superior for multiple bond dissociation.

(ii) Orbital optimization of APSG is more cumbersome than for the Hartree-Fock determinant: there is a considerable danger of ending up in a local minimum. Convergence acceleration has been the subject of a recent study[37].

(iii) Calculation of excited states within the geminal framework is an interesting topic, which was left unexplored until recently[38]. There is certainly room for future studies in this subject.

(iv) Geminal wavefunctions free from the strong orthogonality constraint offer a more flexible description than APSG. Explorations along this line are rare[39–42] but challenging both theoretically and computationally.

(v) For molecules possessing more than one equivalent Lewis structures, the electron pair distribution as used by APSG is ambiguous. Development of models dealing either with more than one limiting structures, or with subunits containing more than 2 electrons, represent challenging issues.

(vi) APSG-based MRPT has not yet been formulated fully diagrammatically.

In concluding, the above points indicate that many further developments are welcome which may enhance the practical applicability of APSG-based multireference techniques. We stress the APSG itself is not a method having sufficient power to describe dynamical correlation, but it is a suitable reference state for several chemical processes. Although it was proposed originally in the early days of quantum chemistry, it was left in a dormant state for several decades. The recent renaissance of these methods offer a promising perspective.

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