Computational and Theoretical Chemistry 1003 (2013) 62–70

Contents lists available at SciVerse ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

Generalized antisymmetric ordered products, generalized normal ordered products, ordered and ordinary cumulants and their use in many electron correlation problem

Debalina Sinha, Rahul Maitra, Debashis Mukherjee *

Raman Center for Atomic, Molecular and Optical Sciences, Indian Association for the Cultivation of Science, Kolkata 700 032, India

ARTICLE INFO

Article history:
Received 6 August 2012
Received in revised form 26 September 2012
Accepted 26 September 2012
Available online 16 November 2012

Keywords:
Cumulants
Generalized normal ordering
Internally Contracted MRCC

ABSTRACT

The use of cumulants in the direct determination of the 2-particle reduced density matrix (2-RDM), Γ_2, via reconstruction schemes where Γ_3 and Γ_4 are expressed in terms of Γ_2 and cumulants to 'close' the hierarchy of density equations of Nakatsuji has been systematically developed for about two decades. A challenging aspect of such developments is the imposition of the N-representability conditions on Γ_2, all of which are not known. Some reasonable sufficiency conditions and the use of the so-called 'weak positivity conditions' have proved to be fruitful but a lot more remains to be done. There is another parallel development involving cumulants where certain 'model cumulants' are extracted from a multi-reference model function Ψ_0 and dynamical correlation is introduced via a wave operator Ω, acting on Ψ_0. The non-dynamical correlation is reflected in the various model cumulants. Such formulations are accomplished in the most compact manner if one uses the notion of generalized normal ordering (GNO) and generalized Wick's theorem (GWT) with respect to Ψ_0. The product of operators in GNO has vanishing expectation value with respect to Ψ_0. The GWT expresses a product of n creation/annihilation operators as a sum of m operators in GNO ($m \leqslant n$) with products of various cumulants along with appropriate phases. This approach, unlike the reconstruction schemes, uses the model cumulants as intermediaries only which are N-representable by construction. In this paper we will introduce the notion of generalized antisymmetrized ordered products (GOPs) and show how a generalized normal ordering for a product of arbitrary number of creation and annihilation operators can naturally emerge as the limit of a hierarchy of GOP. We argue in this paper that the use of GOP leads naturally to the generalized Wick's theorem where the normal ordered products are antisymmetric under permutations and have vanishing expectation values with respect to Ψ_0. We will also show that, except the pair cumulants, all the higher body cumulants have the antisymmetric property and they are equivalent to the cumulants introduced by Kubo. Finally we formulate an explicitly connected (size-extensive) Internally Contracted Multi-reference Coupled Cluster (IC-MRCC) theory with the CAS type of reference function Ψ_0, using the Ansatz for the wave operator Ω as generalized normal ordered exponential of a cluster operator T. The GNO in Ω is with respect to the function Ψ_0. Two different schemes for solving the MRCC equations are proposed. One is a formulation where Ψ_0 is kept frozen as a starting function and only the cluster amplitudes, Ts, are computed. The other is a scheme where the coefficients entering Ψ_0 are relaxed and the coupling with respect to the cluster operators are also included via the MRCC equations. The formulation of the IC-MRCC theories is predicated by the antisymmetric nature of the GNO, which has been explicitly utilized. This completes our earlier program of developing IC-MRCC, where the GNO was exploited but its antisymmetry was implicitly assumed and not proven.

1. Introduction

Ever since Coleman [1], inspired by the challenge of Coulson [2], dwelt incisively on the program of using the 2-particle density matrix Γ_2 as the sole variable to obtain energy directly, side-stepping the knowledge of the eigenfunction Ψ, attempts have been made for more than 50 years now to find out appropriate strategies to achieve this goal. The most challenging task in this endeavor is to find the necessary and sufficient conditions on Γ_2 such that it can be extracted from an N-electron antisymmetric wave-function, which is known in the literature as the famous N-representability problem [1]. Several formal solutions were suggested around the same time as the N-representability problem was pointed out

* Corresponding author.
E-mail address: pcdm@iacs.res.in (D. Mukherjee).

2210-271X/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.comptc.2012.09.035

[3–5]. They were not very useful since, in effect, they required the knowledge of the full N-electron density matrix [5,6]. Nakatsuji in a remarkable paper in 1976 [7] showed that, if for a trial wave function Ψ, $\langle\Psi|C_2H|\Psi\rangle = E\langle\Psi|C_2|\Psi\rangle$ is satisfied, where $E = \langle\Psi|H|\Psi\rangle$ and $\langle\Psi|C_2|\Psi\rangle = \Gamma_2$, then Ψ is an eigenfunction of H. This implied that the hierarchy equations for Γ_n connecting Γ_n with Γ_{n+1} and Γ_{n+2} for all n, derived by Nakatsuji, are automatically satisfied for all $n > 2$, if the above equation holds good. Not much progress for its practical use could be done till the early 1990s, where the hierarchy of the equations for Γ_2 were '*closed*' by approximating the higher body densities as product of the lower body RDMs. This opened up new and powerful ways of using the hierarchies for obtaining energies via Γ_2. Such a scheme was attempted by Valdemoro and her co-workers [8–11]. Nakatsuji and his co-workers [12–14] suggested more accurate reconstruction of Γ_3 and Γ_4 and found improved performance of their scheme. This was further developed via cumulant decomposition of the RDMs by Mazziotti [15–18]. The reconstruction strategy, coupled with certain necessary constraints like the D, Q, G and T_1 and T_2 conditions, have led to rather impressive developments. Very recently, Mazziotti suggested certain hierarchy of N-representability conditions [18,19], whose power and potentiality remain yet to be fully explored. For a comprehensive presentation of the set of ideas related to RDM and cumulants we refer to a volume edited by Mazziotti [20]. While all the efforts mentioned above explored the possibility of using cumulants to reconstruct the few body RDMs such as Γ_2 directly, by suitably approximating Γ_3 and Γ_4 in terms of cumulants, there has been a separate course of development [21,22] where certain 'model' cumulants have been used as building blocks, extracted from a multi-reference 'model' wave function Ψ_0. The non-dynamical correlation in this development is embedded in the model cumulants and the dynamical correlation is incorporated via the action of a wave operator Ω, converting Ψ_0 to the exact function Ψ. Since the model cumulants are derived from a model wave function Ψ_0, the vexing problem of N-representability does not appear in the formulation. The present paper contributes to further exploration along this avenue which sidesteps reconstruction schemes, complementing methods which use cumulants as the target variables using reconstruction schemes.

Use of the model cumulants in the multi-reference context and the concomitant development of the cumulant based many-body theories is predicated by the validity of the concept of generalized normal ordering (GNO) introduced by Mukherjee [23], Kutzelnigg and Mukherjee [24] and further elaborated by Kong *et. al.* [25]. Operators in GNO have vanishing expectation values with respect to the multi-reference model function Ψ_0. The GWT expresses an ordinary product of an arbitrary number n of creation/annihilation operators as a sum of GNO of various m number of operators ($m < n$) with various 'cumulants' containing equal number of creation and annihilation operators, along with various phases. Interestingly, the notion of GNO and the associated Wick-like reduction formula (Generalized Wick's Theorem, GWT [23,24]) can be invoked not only to develop theories bypassing wavefunction via reconstruction formula for RDM [26–30] but also to formulate Internally Contracted Multi-reference Coupled Cluster (IC-MRCC) methods via model cumulants [21,22]. A similar formulation using canonical transformation theory was also suggested later [31–33].

As emphasized above, the present paper will dwell exclusively on the use of cumulants and GNO as convenient intermediaries in an IC-MRCC framework. In particular, our paper will explore and illustrate certain hitherto unanalyzed issues associated with the GNO and the GWT. In contrast to the ordinary normal ordering, where the fermion operators anti-commute inside the normal ordering by its very definition, the operator ordering inside GNO is rather more abstract and the antisymmetry property, analogous to that in the ordinary normal ordering, is not immediately obvious. Similarly, the cumulants generated via the use of GWT also are antisymmetric with respect to the interchange of the order of appearance of the Fermion operators and this remarkable property is also not immediately apparent. Our paper will deal with three important issues associated with GNO and GWT: (a) as a run-up to proving the antisymmetric product nature of GNO and the cumulants, we would introduce the concepts of Generalized Antisymmetric Ordered Products (GAOPs or GOP for a simpler acronym) and emphasize the usefulness of using the GOPs as building blocks to generate GNOs which is a special case of GOP; (b) we also argue in this paper that proving the antisymmetry of the GNO and of the cumulants is essential for developing IC-MRCC theory using cumulants; and (c) after filling in the hitherto missing aspects of the antisymmetry of the GNO and of the cumulants, we will use these properties to formulate two variants of IC-MRCC theory involving cumulants and show that they are extensive by construction. Although, in the earlier developments of IC-MRCC, Mukherjee [21] and Mukherjee and co-workers [22] did make use of the GNO, the property of anti-symmetry in GNO was rather implicit in deriving the working equations but no proof was given.

The paper is organized as follows: In Section 2, we introduce the concepts of GOP, GNO and GWT in an integrated framework. Section 2.1 introduces the notations and discusses the theoretical preliminaries to arrive at the construction of GOP. In Section 2.2 we prove the GWT in terms of suitable hierarchies of GOP and establish the relation between the cumulants generated by the GWT and the cumulants introduced by Kubo [34]. Section 3 explores the development of IC-MRCC using exponential representation of cluster operators in both GOP and GNO form and indicate their extensivity in a systematic manner. Section 4 provides a summary of the developments and our concluding remarks.

2. The notion of generalized antisymmetrized ordered products, ordered and ordinary cumulants, generalized normal ordered products and generalized Wick's theorem

2.1. Theoretical preliminaries

As emphasized in Section 1, there is a major conceptual difference between the ordinary normal ordered product and the GNO. An ordinary normal ordered product by construction has antisymmetry property under permutation of fermion operators in the normal ordering. The time-independent Wick's theorem allows ordinary product of fermion operators as a sum of ordinary normal products with all possible pair contractions and appropriate phase factors. Normal ordered products possess not only the antisymmetry property but also has the property of zero averages with respect to a single determinant 'vacuum' $|\phi\rangle$, used to define the normal ordering. From now on, we will generically use a set of operators $\{q_i\}$ to denote both fermion creation and annihilation operators. For the actual implementation of the normal product algebras, we will of course explicitly specify which of the qs are creation and which are annihilation. The 'contractions' appearing in Wick's theorem are defined as $x_{ij} = \langle\phi|q_iq_j|\phi\rangle$ for a pair of fermion creation/annihilation operators. They are not antisymmetric in the sense that x_{ij} and x_{ji} are not generally negatives of each other. If q_i and q_j are adjoints of each other then $x_{ij} + x_{ji} = 1$. Generally, $x_{ij} + x_{ji} = -\langle\phi|[q_i, q_j]_+|\phi\rangle = N_{ij}$, where N_{ij} is a number, equal to the value of the anticommutator $[q_i, q_j]_+$. In contrast, the time-dependent Wick's theorem [35], as originally developed by Wick, showed how a T-ordered, rather than an ordinary product of a set of creation/annihilation operators can be written as a sum of normal products with all possible contractions. The contractions in the time-dependent Wick's theorem are antisymmetric due to the