Polynomial approximations of electronic wave functions

A. I. Panin

Abstract   This work completes the construction of a purely algebraic version of the theory of finite dimensional electronic Fock spaces endowed with a new law of composition (star product). For a fixed number of electrons the corresponding sector of the Fock space becomes a commutative algebra and its ideals are determined by the excitation level used. New approach to non-linear methods of quantum chemistry based on the systematic use of the star product is developed. Efficient computer implementation of multiplication in the aforementioned algebras is described. Quality of different polynomial approximations of electronic wave functions is illustrated with concrete examples.

Keywords   Fock space · Commutative algebras · Non-linear wave function based methods

1 Introduction

In our previous publications a new law of composition (multiplication) of many electron wave functions was introduced [1,2]. This multiplication is defined with respect to some fixed single determinant p-electron reference state Φ and if such state is selected then product $\Psi_1 *_\Phi \Psi_2$ of two arbitrary p-electron wave functions Ψ_1, Ψ_2 turns out to be *antisymmetric* p-electron wave function. This product posesses four 'good' properties: commutativity, associativity, distributivity with respect to addition, and existence of multiplicative identity. Namely, for any p-electron wave functions Ψ_1, Ψ_2, Ψ_3 the following equalities hold true:

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(i) $\Psi_1 *_\Phi \Psi_2 = \Psi_2 *_\Phi \Psi_1$;
(ii) $(\Psi_1 *_\Phi \Psi_2) *_\Phi \Psi_3 = \Psi_1 *_\Phi (\Psi_2 *_\Phi \Psi_3)$;
(iii) $(\Psi_1 *_\Phi (\Psi_2 + \Psi_3) = \Psi_1 *_\Phi \Psi_2 + \Psi_1 *_\Phi \Psi_3$;
(iv) $\Psi_1 *_\Phi \Phi = \Phi *_\Phi \Psi_1 = \Psi_1$.

p-electron sector of the Fock space endowed with this multiplication becomes a commutative associative algebra with the identity Φ. Notation $\Psi_1 *_\Phi \Psi_2$ seems to be too cumbersome to be used and if it is clear what reference state is under consideration then it is reasonable to supress the subscript Φ by the star product.

In this paper it will be demonstrated that the star product can be introduced on a vector space which already carries the Clifford algebra structure [3–5]. But the properties of algebras endowed with the star product are completely different from the properties of the Clifford algebras.

Additional algebraic structure, especially if it is revealed on such a classic object as the electronic Fock space (Grassmann, or exterior algebra in mathematical terminology) is of interest by itself. For quantum theory, however, possible potential applications of the star product for solving concrete chemical or physical problems are of primary importance.

Direct application of the star product is connected with the well-known fact that on algebras of the discussed type it is easy to define polynomial functions (see, e.g., [6]). For a fixed reference single determinant wave function Φ its orthogonal complement $[\mathbb{K}\Phi]^\perp$ in the space of all p-electron functions will be called *amplitude space*. Here $\mathbb{K}$ is the number field used. Each amplitude τ satisfies the orthogonality condition $\langle \Phi | \tau \rangle = 0$. If by U_Φ we denote subset in p-electron sector of the Fock space containing wave functions Ψ such that $\langle \Phi | \Psi \rangle = 1$ then it is easy to ascertain that each polynomal $P_a(\tau) = \tau^0 + a_1\tau + a_2\tau * \tau + \cdots$ with $\tau^0 = \Phi$ and $a_1 \neq 0$ performs a *parametrization* of the set (surface) U_Φ. Triple $c_\Phi = (U_\Phi, P_a^{-1}, [\mathbb{K}\Phi]^\perp)$ is actually a chart of the *projective* space of p-electron states.

In this way *polynomial approximations* of many electron wavefunctions naturally arise.

General polynomial approximations are closely related to non-linear methods of quantum chemistry of which the Coupled Cluster (CC) method is becoming more and more exploitable replacing till recently very popular methods based on the Multi-Configurational Self Consistent Field (MCSCF) ideology. CC approach was introduced into quantum chemistry by Cizek [7,8] and gained development in numerous publications by Bartlett and Paldus (see [9–15] and references therein). Account of modern state of CC theory was given by Bartlett and Musial in [16].

Polynomial approximations of wave functions described in this paper lead to a new approach to non-linear methods of quantum chemistry. It is pertinent therefore to list the main points in which our approach differs from the CC one:

(i) Polynomial parametrizations naturally appear as soon as new multiplication law is introduced on the Fock space and at that no special anzatz of wave function is required;
(ii) Space of amplitudes is constituted by many electron states belonging to the orthogonal complement to the reference determinant Φ;
(iii) Notion of cluster seems to be irrelevant within our approach;

(iv) All manipulations with creation-annihilation operators based on the Wick the-
      orem become unnecessary since all sign prefactors are incorporated in the def-
      inition of the star product from the very beginning;

(v)   For calculation of excited states instead of Equation-of-Motion (EOM) stan-
      dard Time-Dependent (TD) theory can be developed and the corresponding TD
      equations can be derived.

Note also that simply from the definition of polynomial functions it readily fol-
lows that *any true parametrization covers the whole domain of the chart c_Φ*. In other
words, if exact (Full Configuration Interaction, FCI) wave function has nonzero pro-
jection on the selected reference state, then it can be obtained with the aid of *any
true parametrization*. This means, for example, that simple quadratic parametrization
$q(\tau) = \tau^0 + \tau + \alpha\tau * \tau$ can be used to calculate *exact* wave function and all its dis-
advantages frequently emphasized in literature are connected with concrete selection
of the space of amplitudes but not with the quadratic approximation. The disadvan-
tages of simple parametrizations (quadratic, cubic, etc) manifest itself *only* at the low
excitation levels and readily disappear when the excitation level becomes sufficiently
high.

The problem concerning the possibility of efficient computer implementation of
our technique for quantum chemical calculations is still open. CC approach is imple-
mented at present on a rather efficient level [17]. We can only state that calculation of
polynomial wave function can be elegantly programmed for arbirary excitation level
in the amplitude vector on the base of the well-known revolving door algorithm [18].

In present paper we give a reasonably rigorous description of the algebraic structure
defined by the star product and demostrate that this product can be introduced not only
on the Fock space but also on its quotients. As the first application of the star prod-
uct we study algebraic backgrounds of non-linear methods of quantum chemistry and
on concrete examples compare the quality of different polynomial approximations of
many electron wave functions.

In Sect. 2 the law of composition (star product) of many electron wave functions is
introduced and its properties are discussed.

In Sect. 3 polynomial functions and their inverse are studied.

Section 4 is dedicated to general approach to variational determining of polynomial
expansions and to the corresponding TD equations for calculation of excited states.

In Sect. 5 non-variational approach to determining polynomial wave functions is
briefly outlined. It is the only section having relation to the CC approach.

In Sect. 6 computer implementation of the the star product is discussed.

In Sect. 7 on concrete examples we compare CI expansions with their polynomial
approximations.

2 Formal Fock space

In quantum theory the notion of space of occupation numbers is widely used and
became habitual both to physicists and to quantum chemists (see, e.g., [19,20]). Recall
that if the number of molecular spin orbitals (MSO) is finite and if they are labelled
by indices from the index set $N = \{1, 2, \ldots, n\}$ then the corresponding space of

occupation numbers is generated by bit vectors $(n_1, n_2, \ldots)$ of length n with $n_i = 0(1)$. These bit vectors constitute a basis of 2^n-dimensional vector space and their interpretation is very simple: each bit vector corresponds to *normalized* Slater determinant built on MSOs having non-zero occupancies in the bit vector under consideration. Support of bit vector is defined as a subset of the index set N, involving indices (positions) where occupation number is equal to 1. It is clear that each bit vector is determined by its support and *vice versa*. It is possible therefore to replace bit vectors by their supports and consider linear combinations of all subsets of the index set N.

Definition Vector space of formal linear combinations of all subsets of the index set N with coefficients from the ground field $\mathbb{K}$ will be called the formal Fock space over $\mathbb{K}$ associated with the index set N and will be denoted by the symbol $\mathfrak{F}_N$.

In this work fields of real ($\mathbb{K} = \mathbb{R}$) and complex ($\mathbb{K} = \mathbb{C}$) numbers will be of actual interest.

For each subset $R \subset N$ symbol e_R will stand for a basis vector of the formal Fock space. Of course, e_R is just a notation for a subset of the index set N, playing, as used here, a role of a basis vector.

With each index from the MSO index set creation and annihilation operators can be associated and formal Hamiltonian can be defined in terms of these creation-annihilation operators and 1- and 2-electron integrals as parameters.

The definition of the formal Fock space immediately suggests that one can try to use standard set-theoretic operations (union, intersection, difference, symmetric difference) to introduce in this space new laws of composition in addition to the already existing (addition and multiplication by scalars from $\mathbb{K}$). It should be emphasized that such an approach is widely used in modern mathematics. Namely, first a set with some algebraic operations on it is taken, then vector space of formal linear combinations of elements of this set is constructed and initial algebraic operations are continued by linearity to the space of formal linear combinations. The standard example is a formal linear hull $\mathbb{K}[G]$ of multiplicative group G. Putting

$$\left(\sum_{g \in G} a_g e_g \right) \left(\sum_{h \in G} b_h e_h \right) = \sum_{g,h \in G} a_g b_h e_{gh} \tag{1}$$

we come to the well-known and very important object called group algebra of (finite) group G over $\mathbb{K}$ (see, e.g., [21]).

We start with a law of composition (multiplication) on $\mathfrak{F}_N$ which has been well-known for about 120 years and was first introduced by Clifford [3]. Its modern interpretation may be found in [4,5]. This multiplication is a combination of set-theoretic union of MSO indices and contraction of a certain part of these indices with the aid of some fixed symmetric bilinear form g on '1-electron' space $\mathfrak{F}_N^1$. It is convenient to assume that basis constituted by the vectors $e_i = e_{\{i\}}$ is orthogonal with respect to this form. Then the aforementioned law of composition is defined as [4,5]

$$e_R . e_S = \prod_{\substack{r \in R \\ s \in S}} (r, s) \prod_{i \in R \cap S} g(e_i, e_i) e_{R \triangle S} \tag{2}$$

where $R \Delta S = R \cup S - R \cap S$ and

$$(r, s) = \begin{cases} 1 & \text{if } r \le s \\ -1 & \text{if } r > s \end{cases} \tag{3}$$

and where it is assumed that 'empty' products are equal to 1. In terms of the set-theoretic operation Δ_K [1] the sign prefactor may be written as

$$\prod_{\substack{r \in R \\ s \in S}} (r, s) = (-1)^{|(S-R) \cap \Delta_{(R-S)}|} \tag{4}$$

This presentation of sign prefactor is very convenient both for analytic and numerical purposes. For example, proof of associativity in Clifford-type algebras becomes practically automatic.

Directly from definition it follows that $e_{\emptyset}$ is the identity element of the multiplication (2). It is easy to show that this law of composition is associative, non-commutative, and endows the formal Fock space with the Clifford algebra structure. Classic relation

$$x.y + y.x = 2g(x, y)e_{\emptyset}, \tag{5}$$

valid for any elements $x, y \in \mathfrak{F}_N^1$, is readily obtained from Eq. (2).

If g is zero form then the Clifford algebra is just a Grassmann algebra of '1-electron' space $\mathfrak{F}_N^1$.

Another type of multiplications on the formal Fock space was introduced in our previous publications [1,2]. Recall briefly most important definitions.

For any fixed subset $R \subset N$ ('reference subset') basis vectors of the formal Fock space may be written as $e_J^I(R) = e_{R-J \cup I}$ where $J \subset R, I \subset N - R$. Law of composition of these basis vectors ('star product') is defined as (see [1])

$$e_J^I(R) * e_{J'}^{I'}(R) = \begin{cases} \left[\prod_{\substack{r \in I \cup J \\ s \in I' \cup J'}} (r, s) \right] e_{J \cup J'}^{I \cup I'}(R) & \text{if } (I \cup J) \cap (I' \cup J') = \emptyset, \\ 0 & \text{if } (I \cup J) \cap (I' \cup J') \ne \emptyset \end{cases} \tag{6}$$

Relations (6) constitute the multiplication table of an algebra and it is easy to ascertain that this algebra is associative, skew-commutative, and that $e_{\emptyset}^{\emptyset}(R) = e_R$ is its identity element. Skew-commutativity readily follows from the equality

$$e_J^I(R) * e_{J'}^{I'}(R) = (-1)^{|J \cup I| \cdot |J' \cup I'|} e_{J'}^{I'}(R) * e_J^I(R) \tag{7}$$

In the finite-dimensional case we have 2^n ways to select reference subset and, consequently, 2^n different multiplications on the formal Fock space. Of course, algebras, corresponding to reference subsets with the same number of electrons are isomorphic.

The simplest reference subset is $R = \emptyset$ and the corresponding basis vectors are $e_\emptyset^I(\emptyset) = e_I$. We have the following relations

$$e_\emptyset^I(\emptyset) * e_\emptyset^{I'}(\emptyset) = \begin{cases} \left[\displaystyle\prod_{\substack{r \in I \\ s \in I'}} (r, s) \right] e_\emptyset^{I \cup I'}(\emptyset) & \text{if } I \cap I' = \emptyset, \\ 0 & \text{if } I \cap I' \neq \emptyset \end{cases} \tag{8}$$

which constitute the multiplication table of the Grassmann algebra. In this particular case the star product is just the classic Grassmann exterior product.

If the reference subset R belongs to the p-electron sector of the formal Fock space ($|R| = p > 0$) and $|I| = |J| = r \leq \min\{p, n - p\}$ then, as immediately follows from Eq. (7), the star product endows this sector with the *commutative* algebra structure. As it will be shown later, this structure is particularly important for quantum chemistry. Unless otherwise stated, from here on only p-electron sector $\mathfrak{F}_N^p$ of the formal Fock space will be under consideration. For fixed p-element subset R the commutative p-electron algebra with the identity e_R will be denoted $A_N^p(R)$. Its basis elements are $e_J^I(R)$ with $|J| = |I| = l$ where l is the so-called *excitation order or excitation level* ($l = 0, 1, \ldots, \min\{p, n - p\}$).

Algebra $A_N^p(R)$ admits a decomposition into a direct sum of subspaces

$$A_N^p(R) = \bigoplus_{l \in \mathbb{Z}} V_N^l(R) \tag{9}$$

where

$$V_N^l(R) = \overset{(l)}{\underset{\substack{J \subset R \\ I \subset N - R}}{\bigoplus}} \mathbb{K} e_J^I(R) \tag{10}$$

and where $V_N^l(R) = \{0\}$ for $l < 0$ and $l > \min\{p, n - p\}$. In the last equation the summation goes over all l - element subsets of the index sets R and $N - R$, and this is denoted by the upper index (l) over the sum symbol. For fixed $1 \leq l \leq \min\{p, n - p\}$ this subspace can be called 'subspace of all excitation of order l from the reference subset R'. From the definition of the star product it readily follows that

$$V_N^k(R) * V_N^l(R) \subset V_N^{k+l}(R) \tag{11}$$

which means that $A_N^p(R)$ is *a $\mathbb{Z}$-graded algebra*.

Subspace

$$I_N^r(R) = \bigoplus_{l=r+1}^{\min\{p, n-p\}} V_N^l(R) \tag{12}$$

is an ideal of $A_N^p(R)$ for any $r \geq 0$. This means that any quotient space $A_N^p(R)/I_N^r(R)$ is also a commutative algebra with the law of composition

$$[\Psi_1 * \Psi_2]_r = [\Psi_1]_r * [\Psi_2]_r \tag{13}$$

where $[\Psi]_r = \Psi + I_N^r(R)$. By an abuse of language the star product in the quotient algebra $A_N^p(R)/I_N^r(R)$ will be called 'star product modulo r'.

It is clear that $I_N^0(R)$ is *a maximal nilpotent ideal* of $A_N^p(R)$. Maximality means that it is not contained in any ideal of the algebra under consideration and nilpotency means that $\left[I_N^0(R)\right]^r = I_N^0(R) * \ldots * I_N^0(R) = \{0\}$ for $r > \min\{p, n - p\}$.

$A_N^p(R)$ is an abstract model of a typical full Configuration Interaction (CI) space (endowed with the additional multiplication) devoid of any orbital specificity. Vectors from the vector space

$$W_N^r(R) = \bigoplus_{l=1}^{r} V_N^l(R) \tag{14}$$

will be called amplitudes. *Note that in contrast to the standard CC type methods our amplitudes are just wave functions from the same p-electron sector of the Fock space.*

If $\mathcal{F}^1$ is a concrete 1-electron space and $\psi = (\psi_1, \psi_2, \ldots, \psi_n)$ is some its orthonormal n-frame of MSOs, then the *substitution mapping*

$$s_\psi : e_R \mapsto \psi_{i_1} \wedge \psi_{i_2} \wedge \cdots \wedge \psi_{i_p}, \tag{15}$$

where $R = \{i_1, i_2, \ldots, i_p\}, i_1 < i_2 < \cdots < i_p$ establishes (basis-dependent) isomorphism between the formal Fock space $\mathfrak{F}_N$ and the concrete Fock space $\mathcal{F}$. The substitution mapping can also be used to transfer the algebra structures defined by Eq. (6) from the formal Fock space to any of its concrete realizations. The inverse mapping s_ψ^{-1} (also basis dependent) strips vectors of a concrete Fock space of their orbital specificity.

It is pertinent to emphasize that for any concrete realization of the Fock space the star product of arbitrary p-electron wave functions is (an antisymmetric) p-electron wave function.

At this stage it is reasonable to give a definition of the star product in terms habitual to quantum chemists. Let $\Phi = \psi_1 \wedge \psi_2 \wedge \cdots \wedge \psi_p$ be some reference Slater determinant and orthonormal basis of the p-electron sector of the Fock space is taken in the form of all possible 'excited' determinants $\Phi_{j_1 j_2 \ldots j_l}^{i_1 i_2 \ldots i_l}$. MSOs with indices $J = \{j_1 < j_2 < \ldots < j_l\}$ are occupied in the reference determinant, and MSOs with indices $I = \{i_1 < i_2 < \ldots < i_l\}$ are the virtual ones. Then the star product of two basis determinants is defined as

$$\Phi_J^I * \Phi_{J'}^{I'} = \begin{cases} (-1)^\varepsilon \Phi_{J \cup J'}^{I \cup I'} & \text{if } (J \cup J') \cap (I \cup I') = \emptyset \\ 0 & \text{if } (J \cup J') \cap (I \cup I') \neq \emptyset \end{cases} \tag{16}$$

The definition of the sign prefactor in this expression is of primary importance because the possibility to introduce on the Fock space a new amultiplication law is a direct consequence of this definition. We illustrate the calculation of the sign prefactor on a simple example. Let us consider 10-electron system and the product

$$\Phi_{2,4,6}^{11,13,15} * \Phi_{1,3,5}^{10,12,14} = (-1)^\varepsilon \Phi_{1,2,3,4,5,6}^{10,11,12,13,14,15}$$

where the sign prefactor is

$$\left[\prod_{\substack{r\in\{2,4,6,11,13,15\}\\ s\in 1,3,5,10,12,14}} (r,s)\right] = (-1)^{21} = -1$$

In terms of the aforementioned set-theoretic operation Δ_K, a much more elegant way of sign prefactor calculation may be suggested. The expression for ε is

$$\varepsilon = |(J' \cup I') \cap \Delta_{(J\cup I)}| \tag{17}$$

and in the particular case under discussion $(J' \cup I') \cap \Delta_{(J\cup I)} = \{3, 10, 14\}$ which gives $\varepsilon = 3$. Note that besides polynomial approximation of wave functions the star product may be used, for instance, to construct wave function of a system from wave functions of its selected subsystems and the resulting product will automatically be antisymmetric.

The formal Fock space can be endowed with the Euclidean ($\mathbb{K} = \mathbb{R}$) or the Hermitian ($\mathbb{K} = \mathbb{C}$) structure in a simple and natural way:

$$\langle e_R | e_{R'} \rangle = \begin{cases} 1 & \text{if } R = R' \\ 0 & \text{if } R \neq R' \end{cases} \tag{18}$$

If a concrete 1-electron Fock space is a vector space with the inner product and ψ is some its orthonormal (with respect to this inner product) n-frame then the substitution mapping is obviously isometric.

The group of orthogonal (or unitary) transformations of 1-electron Fock space $\mathcal{F}^1$ will be denoted $\mathcal{G}(\mathcal{F}^1)$. If ϖ_R is a p-plane (p-dimensional subspace) of 1-electron Fock space spanned by MSO $\{\psi_i\}$, $i \in R$ and $\varpi_R^\perp$ is its orthogonal complement then for any block-diagonal transformation $U \in \mathcal{G}(\varpi_R) \times \mathcal{G}(\varpi_R^\perp)$

$$s_\psi(V_N^l(R)) = s_{\psi U}(V_N^l(R)) \tag{19}$$

where $l = 0, 1, \ldots, \min\{p, n - p\}$. In the case $l = 0$ this equality is equivalent to the well-known property of the determinant states: each determinant state is defined up to an arbitrary orthogonal (unitary) transformation of occupied (virtual) MSOs. Therefore, Eq. (19) may be considered as a generalization of this simple property of determinants. It is to be noted that, in general, $s_\psi(\tau) \neq s_{\psi'}(\tau)$ for *concrete* non-zero

vector $\tau \in \mathrm{V}_N^l(R)$. However, Eq. (19) and the accompanying group-theoretical arguments will become actually important only if a general theory including optimization of both amplitudes and MOs is under consideration.

3 Polynomial functions with algebra $\mathrm{A}_N^p(R)$ as their range

Many methods of quantum chemistry may be uniformly described in terms of polynomial functions $P_a : \mathrm{W}_N^r(R) \to \mathrm{A}_N^p(R)$ of the form

$$P_a(\tau) = \sum_{\mu=0}^{\min\{p,n-p\}} a_\mu \tau^\mu \tag{20}$$

where $a_i \in \mathbb{K}$, $\tau^\mu = \underbrace{\tau * \cdots * \tau}_{\mu \text{ times}}$, and $\tau^0 = e_\emptyset^\emptyset(R)$. Since $\mathrm{W}_N^r(R)$ is a subspace of the nilpotent ideal $\mathrm{I}_N^0(R)$, all polynomial functions of the type of Eq. (20) have degrees not greater than $\min\{p, n - p\}$.

Using polynomial functions it is easy to characterize invertible elements of algebra $\mathrm{A}_N^p(R)$.

Proposition *Wave function Ψ is an invertible element of algebra $\mathrm{A}_N^p(R)$ if and only if $a_0 = \langle \Psi | e_\emptyset^\emptyset(R) \rangle \neq 0$.*

Proof Let us put $\tau = \Psi - a_0 e_\emptyset^\emptyset(R)$. By direct calculation it is easy to ascertain that

$$\Psi^{-1} = \sum_{\mu=0}^{\min\{p,n-p\}} (-1)^\mu \frac{\tau^\mu}{a_0^{\mu+1}} \tag{21}$$

$\square$

Corollary *Amplitude vectors are not invertible.*

To illustrate the notion of the inverse element in algebra $\mathrm{A}_N^p(R)$ let us consider wave function $\Psi = a_0 \bar{\tau}^0 + a_1 \bar{\tau}$ with $a_0 \neq 0$. The inverse wave function is

$$\Psi^{-1} = \frac{1}{a_0} \left[e_\emptyset^\emptyset(R) - \frac{a_1}{a_0} \bar{\tau} + \left(\frac{a_1}{a_0} \bar{\tau} \right)^2 - \ldots \right] \tag{22}$$

Polynomial functions $P_a(\tau)$ such that (1) $a_0 \neq 0$, and (2) $P_a(\tau)$ are injective, are most important for applications in quantum chemistry. The first condition means that for any amplitude vector τ the state vector $P_a(\tau)$ has a non-zero projection on the reference basis vector $e_\emptyset^\emptyset(R)$, and, consequently, is invertible. Without loss of generality we can put $a_0 = 1$. The second condition guarantees that the mapping $\tau \to P_a(\tau)$ is *a parametrization of the surface* $\mathcal{S}_N^r(R) = P_a\left(\mathrm{W}_N^r(R)\right)$ in the algebra $\mathrm{A}_N^p(R)$

of p-electron states. The dimension of this surface is equal to the dimension of the amplitude space $W_N^r(R)$.

Proposition *Inverse of a polynomial function $P_a(\tau) : W_N^r(R) \to \mathcal{S}_N^r(R)$ is also a polynomial function and it exists if and only if $a_1 \neq 0$.*

Proof Follows directly from the recurrence formulas for the coefficients of the inverse polynomial $P_a^{-1}(a_0 e_\emptyset^\emptyset(R) + \tau) = \sum_{\mu=1} (-1)^{\mu-1} b_\mu \tau^\mu$:

$$b_\mu = \frac{(-1)^\mu}{a_1^\mu} \sum_{\nu=1}^{\mu-1} (-1)^{\nu-1} b_\nu \sum_{i_1+\cdots+i_\nu=\mu} a_{i_1} \cdots a_{i_\nu}, \tag{23a}$$

$$b_1 = \frac{1}{a_1}. \tag{23b}$$

$\square$

Note that invertibility of $P_a(\tau)$ is equivalent to the condition that the polynomial derivative

$$P_a'(\tau) = \left(\sum_{\mu=0}^{\min\{p,n-p\}} a_\mu \tau^\mu \right)' = \sum_{\mu=1}^{\min\{p,n-p\}} \mu a_\mu \tau^{\mu-1} \tag{24}$$

is non-zero for any amplitude vector τ as could be expected.

It is pertinent to emphasize that care should be taken to distinguish invertible elements in algebra $A_N^p(R)$ and invertible polynomials.

For any reference subset R and any polynomial function $P_a(\tau)$ with non-zero a_0 and a_1 a triple $c_R = \left(\mathcal{S}_N^r(R), [P_a]^{-1}, W_N^r(R) \right)$ is a chart of a geometric object which can be called *polynomial manifold*. Note that any point of the surface $\mathcal{S}_N^r(R)$ is invertible in algebra $A_N^p(R)$. If wave function Ψ belongs to the surface $\mathcal{S}_N^r(R)$ then Ψ^{-1} belongs to the surface which can be called 'surface of inverse elements of $\mathcal{S}_N^r(R)$' and, by a certain abuse of language, will be called surface inverse to $\mathcal{S}_N^r(R)$. *Thus, each polynomial surface (manifold) arises in pair with its inverse.*

It is pertinent to note that for a fixed polynomial parametrization all arising surfaces form a chain

$$\mathcal{S}_N^1(R) \subset \mathcal{S}_N^2(R) \subset \cdots \subset \mathcal{S}_N^{\min\{p,n-p\}}(R) \tag{25}$$

and, consequently, any surface $\mathcal{S}_N^r(R)$ can be treated as a subsurface of $\mathcal{S}_N^{r'}(R)$ for any $r' > r$. As a result, it is possible to take some reference τ_0 corresponding to a fixed linear combination of determinants and involving certain excitations of *arbitrary* order from the reference subset R. Considering $P_a(\tau_0)$ as the origin, it is possible to construct parametrizations of the type $\tau \mapsto P_a(\tau_0) * P_a(\tau)$ where τ include all excitations up to preferable maximal order r. If $\tau_0 = 0$, we come to the standard polynomial

parametrization. Such an approach presupposes that τ_0 is sparse to be kept in fast memory.

Of *infinitely many* polynomial functions we consider only three types. The first type is certainly the affine function

$$P_{CI} : \tau \rightarrow e_\emptyset^\emptyset(R) + \tau, \qquad P_{CI}^{-1} : e_\emptyset^\emptyset(R) + \tau \rightarrow \tau \tag{26}$$

which corresponds to the CI approach accounting all excitations up to order r from the reference index set R. The corresponding surface $\mathcal{SC}_N^r(R) = P_{CI}\left(\mathrm{W}_N^r(R)\right)$ is just *the affine plane* $e_\emptyset^\emptyset(R) + \mathrm{W}_N^r(R)$. The inverse surface is

$$\tau \mapsto \sum_{k=0}^{\min\{p,n-p\}} (-1)^k \tau^k \tag{27}$$

The second type is the exponential function

$$\exp : \tau \rightarrow \sum_{\mu=0}^{\min\{p,n-p\}} \frac{\tau^\mu}{\mu!}, \quad \exp^{-1} : e_\emptyset^\emptyset(R) + x \rightarrow \sum_{\mu=1}^{\min\{p,n-p\}} (-1)^{\mu-1}\frac{x^\mu}{\mu} \tag{28}$$

The exponential surface $\mathcal{SE}_N^r(R) = \exp\left(\mathrm{W}_N^r(R)\right)$ coincides with its inverse and is, in fact, *a multiplicative Abelian group*.

And the last, third type is

$$q_\alpha : \tau \mapsto e_\emptyset^\emptyset(R) + \tau + \alpha\tau^2, \quad q_\alpha^{-1} : e_\emptyset^\emptyset(R) + x \rightarrow x - \alpha x^2 + 2\alpha^2 x^3 + \cdots \tag{29}$$

corresponding to the alternative formulation of the quadratic CI (QCI) method [22]. With such a parametrization calculation of polynomial value can be done very fast but to reach reasonable precision in approximation of wave function the excitation level should be sufficiently high.

Parametrization closely related to the resolvent mapping in algebra $\mathrm{A}_N^p(R)$ can also be used

$$Q : \tau \rightarrow \sum_{i=0}^{\min\{p,n-p\}} \tau^i, \qquad Q^{-1} : e_\emptyset^\emptyset(R) + x \rightarrow \sum_{\mu=1}^{\min\{p,n-p\}} (-1)^{\mu-1} x^\mu \tag{30}$$

It is easy to see that surfaces $\mathcal{SQ}_N^r(R) = Q\left(\mathrm{W}_N^r(R)\right)$ *and* $\mathcal{SC}_N^r(R)$ *are mutually inverse.*

If $r = \min\{p, n - p\}$ then *any* injective polynomial function may be used to parametrize *all* p-electron states that have non-zero projection on the reference basis vector $e_\emptyset^\emptyset(R)$. This means that from the variational viewpoint all the aforementioned polynomial parametrizations are equivalent. If $r < \min\{p, n-p\}$ then different polynomial functions parametrize different *low dimensional surfaces* in the space of all

p-electron states and correspond, in general, to different variational methods. *In this case the choice of appropriate polynomial parametrization is of primary importance*.

4 Variational methods on polynomial surfaces

In this section, unless otherwise indicated, it will be supposed that the reference index set R is fixed, and symbol R in all expressions will be supressed.

For arbitrary polynomial function $P_a(\tau)$ the electronic energy expression may be written in two equivalent forms:

$$E_a(\tau) = \frac{\langle P_a(s_\psi(\tau)) | H | P_a(s_\psi(\tau)) \rangle}{\| P_a(\tau) \|^2} \tag{31a}$$

$$E_a(\tau) = \frac{\langle P_a(\tau) | H_\psi | P_a(\tau) \rangle}{\| P_a(\tau) \|^2} \tag{31b}$$

where ψ is arbitrary n-frame of $\mathcal{F}^1$, H is the standard p-electron Hamiltonian, and H_ψ is its *formal* parametric analogue expressed via *formal* creation-annihilation operators

$$H_\psi = \sum_{i,j=1}^{n} \langle \psi_i | h | \psi_j \rangle a_i^\dagger a_j + \frac{1}{2} \sum_{i,j,k,l=1}^{n} \langle \psi_i \psi_j | \psi_k \psi_l \rangle a_i^\dagger a_j^\dagger a_l a_k \tag{32}$$

Remember that s_ψ is isometry and, consequently, $\| P_a(s_\psi(\tau)) \|^2 = \| P_a(\tau) \|^2$.

Unless otherwise indicated, the energy expression (31b) will be used.

To get energy stationary conditions, it is necessary to find out interrelation between the star product and derivation. For $\mathbb{K} = \mathbb{R}$ the electronic energy is an analytic function of amplitudes whereas for $\mathbb{K} = \mathbb{C}$ it is not. However, the realification of the complex amplitude space improves the situation. Let us put

$$\tau = \sum_{l=1}^{r} \sum_{\substack{J \subset R \\ I \subset N-R}}^{(l)} (x_J^I + \mathbf{i} y_J^I) e_J^I = x + \mathbf{i} y \tag{33}$$

Then

$$\frac{\partial}{\partial x_J^I} P_a(\tau) = P_a'(\tau) * e_J^I, \qquad \frac{\partial}{\partial y_J^I} P_a(\tau) = \mathbf{i} P_a'(\tau) * e_J^I \tag{34}$$

and

$$\frac{\partial E_a}{\partial x_J^I}(\tau) = \frac{2}{\| P_a(\tau) \|^2} \mathrm{Re} \langle P_a'(\tau) * e_J^I | H_\psi - E_a(\tau) \hat{I} | P_a(\tau) \rangle \tag{35a}$$

$$\frac{\partial E_a}{\partial y_J^I}(\tau) = \frac{2}{\| P_a(\tau) \|^2} \mathrm{Im} \langle P_a'(\tau) * e_J^I | H_\psi - E_a(\tau) \hat{I} | P_a(\tau) \rangle \tag{35b}$$

where the expression for polynomial derivative $P_a'(\tau)$ is given by Eq. (24).

Now we can write down the stationary conditions for electronic energy as a function on the surface $\mathcal{S}_N^r$:

$$\langle P_a'(\tau) * e_J^I | H_\psi - E_a(\tau)\hat{I} | P_a(\tau)\rangle = 0 \tag{36}$$

where $J \subset R, I \subset N - R, |J| = |I| = 1, 2, \ldots, r$.

Wave functions $P_a'(\tau) * e_J^I$ and $\mathbf{i} P_a'(\tau) * e_J^I$ are linearly independent forming a basis of the realified tangent space $\mathsf{T}_{P_a(\tau)}\mathcal{S}_N^r$ to the surface $\mathcal{S}_N^r$ at the point $P_a(\tau)$.

In the particular case of $P_a(\tau) = e_\emptyset^\emptyset + \tau$ the system (36) is equivalent to the eigenvalue problem for the projection of the electronic Hamiltonian on the subspace spanned by the basis vectors e_J^I with $0 \le |I| = |J| \le r$ (CI method accounting all excitations up to order r from the reference determinant). In general case the system (36) can be reduced to the eigenvalue problems for electronic Hamiltonian projection on τ - dependent subspace spanned by vector $P_a(\tau)$ and tangent vectors $P_a'(\tau) * e_J^I$. Since these vectors are not orthogonal, non-trivial Gram (overlap) matrix arises and the aforementioned eigenvalue problem is actually a generalized one.

At this stage we can see the advantages of the exponential parametrization. First, calculation of the polynomial derivative is not required because $\exp'(\tau) * e_J^I = \exp(\tau) * e_J^I$. Second, algorithm for τ update is very simple and efficient and can be described as follows.

(i) For a fixed amplitude vector τ generalized eigenvalue problem for the Hamiltonian projection on subspace spanned by vectors $\exp \tau * e_J^I$ with $0 \le |J| = |I| \le r$ is solved to give the ground state vector

$$\Psi(\tau) = c_0 \exp(\tau) + \sum_{l=1}^{r} \sum_{\substack{J \subset R \\ I \subset N-R}}^{(l)} c_J^I \exp(\tau) * e_J^I \tag{37}$$

(ii) After dividing by c_0 wave function is rewritten in the form

$$\Psi(\tau) = \exp(\tau + \Delta\tau) \tag{38}$$

where

$$\Delta\tau = log\left(e_\emptyset^\emptyset + \sum_{l=1}^{r} \sum_{\substack{J \subset R \\ I \subset N-R}}^{(l)} c_J^I e_J^I\right) \tag{39}$$

(iii) If $\|\Delta\tau\|$ is still greater than some threshold value, we put $\tau \leftarrow \tau + \Delta\tau$ and return to step (i).

At each step of this algorithm energy value never rises. Note that at step (ii) we used the fact that the exponent is an isomorphism of the additive group of amplitudes onto the multiplicative group $\mathcal{S}E_N^r$. For arbitrary polynomial parametrization the analogous algorithm is more complicated.

In the same simple manner it is possible to derive linearized equations for system evolution on arbitrary polynomial surface *in the vicinity of electronic energy stationary point*. To this end we should first get the formula for the electronic energy second derivatives assuming that the ground field is $\mathbb{C}$. Realification of the amplitude space and calculation of the second energy derivatives with respect to real variables x, y give

$$D^2 E_a(x, y) = \frac{2}{\|P_a(\tau)\|^2}$$
$$\times \begin{pmatrix} \mathrm{Re}\left[(\mathrm{H} + \Delta) - E\,(\mathrm{G} + \mathrm{S})\right] & -\mathrm{Im}\left[(\mathrm{H} + \Delta) - E\,(\mathrm{G} + \mathrm{S})\right] \\ \mathrm{Im}\left[(\mathrm{H} - \Delta) - E\,(\mathrm{G} - \mathrm{S})\right] & \mathrm{Re}\left[(\mathrm{H} - \Delta) - E\,(\mathrm{G} - \mathrm{S})\right] \end{pmatrix} \tag{40}$$

where

$$\mathrm{H}_{JI,J'I'} = \langle P_a'(\tau) * e_J^I | H | P_a'(\tau) * e_{J'}^{I'} \rangle \tag{41a}$$

$$\mathrm{G}_{JI,J'I'} = \langle P_a'(\tau) * e_J^I | P_a'(\tau) * e_{J'}^{I'} \rangle \tag{41b}$$

$$\Delta_{JI,J'I'} = \langle P_a(\tau) | H | P_a''(\tau) * e_J^I * e_{J'}^{I'} \rangle \tag{41c}$$

$$\mathrm{S}_{JI,J'I'} = \langle P_a(\tau) | P_a''(\tau) * e_J^I * e_{J'}^{I'} \rangle \tag{41d}$$

Here H is a Hermitean matrix representing one of two identical blocks of projection of the electronic Hamiltonian on the realified tangent space to the surface $\mathcal{S}_N^r$ at a point $P_a(\tau)$, G is a Hermitean Gram (overlap) matrix of, in general non-orthogonal, basis $\{P_a'(\tau) * e_J^I\}$, Δ and S are *symmetric* matrices arising due to non-zero curvature of the aforementioned surface.

Using standard technique based on the theory of Hamiltonian equations on symplectic manifolds (see, e.g. [23–29]), it is easy to derive the following linearized evolution equation in variables τ, $\bar{\tau}$ (Schrödinger form)

$$\begin{pmatrix} \dot{\tau} \\ \dot{\bar{\tau}} \end{pmatrix} = \frac{i}{\|P_a(\tau_0)\|^2} \begin{pmatrix} \mathrm{H} - E_a(\tau_0)\mathrm{G} & \bar{\Delta} - \bar{S} \\ -(\Delta + S) & -(\bar{\mathrm{H}} - E_a(\tau_0)\bar{\mathrm{G}}) \end{pmatrix} \begin{pmatrix} \tau \\ \bar{\tau} \end{pmatrix} \tag{42}$$

where τ_0 is *electronic energy stationary point*, matrices H, G, Δ and S are calculated at this point, and the amplitude vector τ in this equation is just the replacement vector from τ_0. In quantum chemistry such an approach to calculation of transition energies is called time-dependent (TD). Thus, system (42) embraces all versions of TD methods based on polynomial parametrizations.

In simple case of parametrization $P_{CI}(\tau) = e_\emptyset^\emptyset + \tau$ Gram matrix reduces to the identity matrix, matrices Δ and S just vanish. And as could be expected, TDCI method, due to zero curvature of the surface $\mathcal{SC}_N^r$, gives nothing new in comparison with the linear CI approach.

In conclusion to this section it is pertinent to give a very brief outline of a possible generalization of the variational problem under discussion. If MOs are to be varied, then the electronic energy domain may be elegantly described as a (locally trivial) vector bundle with Grassmann manifold over 1-electron sector of the Fock space as

its base and the formal amplitude vector space as a typical fibre. Such an approach embraces Hartree-Fock (HF) case (zero typical fibre) and MCSCF methods along with the already discussed ones, and all relevant TD methods.

At the present stage of development fully variational non-linear methods are considered as unfeasible. The reason is in problems with the Hamiltonian matrix element evaluation. Even if the current amplitude vector τ is of a reasonably small length to be kept in fast memory, full CI expansion of $P_a(\tau)$ required for matrix element evaluation may be of huge size and level of complexity of matrix element evaluation is close to that in the FCI method. One of the approaches which may help in avoiding this bottleneck is the following. It is possible to get complicated but closed analytic expression for vector $H P_a(\tau)$ *without preliminary FCI expansion of $P_a(\tau)$*. Arising on this way overlap-type matrix elements can be handled recurrently also without explicit CI expansions. However, this is only a hint for possible future developments.

5 Polynomial functions with quotient algebras as their range

For each fixed excitation level r and each polynomial $P_a : W_N^r(R) \to A_N^p(R)$ we can consider the function $P_a^r : W_N^r(R) \to A_N^p(R)/I_N^r(R)$ defined as

$$P_a^r : \tau \mapsto [P_a(\tau)]_r \tag{43}$$

Using star multiplication in quotient algebra, we can write

$$P_a^r(\tau) = \sum_{\mu=0}^{r} a_\mu [\tau^\mu]_r = \sum_{\mu=0}^{r} a_\mu [\tau]_r^\mu \tag{44}$$

Note that for calculation of polynomial value in the quotient algebra only the first $r + 1$ coefficients a_μ are required. If $a_1 \neq 0$ then the inverse polynomial $[P_a^r]^{-1}$ exists and its coefficients $b_1, b_2, \ldots, b_r$ can be calculated using general Eq. (23) ($b_0 = 0$ by definition).

Since the Fock space is equipped with the inner product (see Eq. 18), we can identify quotient space $A_N^p(R)/I_N^r(R)$ with the orthogonal complement to $I_N^r(R)$ which is just the subspace $\mathbb{K}e_\emptyset^\emptyset(R) \oplus W_N^r(R)$.

Strictly speaking, for a fixed polynomial parametrization $P_a(\tau)$ the Schrödinger equation

$$H P_a(\tau) = E P_a(\tau) \tag{45}$$

has a solution if and only if

  (i)   the exact eigenfunction of the electronic Hamiltonian H has non-zero projection on the chosen reference subset R;
  (ii) the excitation level is sufficiently high (ideally $r = \min\{p, n - p\}$).

In other words, the eigenvector should belong to the polynomial surface S_N^r. In practice, however, relatively low excitations levels are used. This means that we can

hardly hope to find amplitude vector, satisfying Eq. (45). But it is possible to consider quotient Schrödinger equation in quotient algebra

$$[HP_a(\tau)]_r = E_a^r(\tau)[P_a(\tau)]_r \qquad (46)$$

which can be recast in the following more habitual form

$$\langle e_J^I | HP_a(\tau) \rangle = E_a^r(\tau) \langle e_J^I | P_a(\tau) \rangle \qquad (47)$$
$$(J \subset R, I \subset N - R, 0 \le |J| = |I| \le r)$$

The number of scalar equation in this system is $\dim[W_N^r(R)] + 1$, that is exactly the number of unknowns (amplitude vector coordinates) plus 1. One additional equation corresponds to $J = I = \emptyset$ and is used to evaluate 'energy' value for a fixed τ:

$$E_a^r(\tau) = \frac{\langle e_\emptyset^\emptyset | HP_a(\tau) \rangle}{a_0} \qquad (48)$$

With such an approach 'energy' E_a^r depends both on the parametrization (polynomial coefficients a) and excitation level (r), not being variational. It tends to the exact value when $r \to \min\{p, n - p\}$ *independently of* a.

Iterative solution of the linearized system (47) is normally used in CC type calculations (see, e.g., [16]). One can try as well to solve iteratively the initial vector equation (46) rewriting it in the form

$$[\tau]_r = [P_a^r]^{-1} \left(\frac{[HP_a(\tau)]_r}{E_a^r(\tau)} \right) = b_1 \frac{[HP_a(\tau)]_r}{E_a^r(\tau)} + b_2 \left[\frac{[HP_a(\tau)]_r}{E_a^r(\tau)} \right]^2 + \cdots \quad (49)$$

In concluding this section it is pertinent to note that, when solving the aforementioned equations, the main problem arising is the calculation of vector $[HP_a(\tau)]_r$ required at each iteration. To perform such a calculation CI expansion of the polynomial function $P_a(\tau)$ up to excitation level $r + 2$ is required. Using the star product, we can instead derive formulas for direct action of creation-annihilation operator products on polynomial functions.

6 Computer implementation of star product in quotient algebras

When using polynomial parametrization, one of the crucial points is the calculation of the star product of two wave functions modulo r. Since almost all calculations in quantum chemistry are performed in MO representation, from the very beginning we separate α- and β-indices and replace MSO index sets by pairs of MO index sets. In particular, MSO index set N will be replaced by a pair (M, M) of α- and β-index sets, $|M| = m$, reference subset R will become the pair (R_α, R_β), and basis elements of algebra $A_{(M,M)}^{(p_\alpha, p_\beta)}(R_\alpha, R_\beta)$ will be $e_{J_\alpha, J_\beta}^{I_\alpha, I_\beta}(R_\alpha, R_\beta)$. In what follows, unless otherwise indicated, it will be supposed that the reference pair of index sets (R_α, R_β) is fixed, and in all expressions dependence on (R_α, R_β) will be suppressed.

Let us present classes of wave functions modulo r to be $*$-multiplied in the standard form

$$[\Psi]_r = I^r + \sum_{k=0}^{r} \sum_{k_\alpha} \sum_{\substack{J_\alpha \subset R_\alpha \\ I_\alpha \subset M - R_\alpha}}^{(k_\alpha)} \sum_{\substack{J_\beta \subset R_\beta \\ I_\beta \subset M - R_\beta}}^{(k_\beta)} e_{J_\alpha, J_\beta}^{I_\alpha, I_\beta} x_{J_\alpha, J_\beta}^{I_\alpha, I_\beta} \tag{50a}$$

$$[\Phi]_r = I^r + \sum_{k=0}^{r} \sum_{k_\alpha} \sum_{\substack{J_\alpha \subset R_\alpha \\ I_\alpha \subset M - R_\alpha}}^{(k_\alpha)} \sum_{\substack{J_\beta \subset R_\beta \\ I_\beta \subset M - R_\beta}}^{(k_\beta)} e_{J_\alpha, J_\beta}^{I_\alpha, I_\beta} y_{J_\alpha, J_\beta}^{I_\alpha, I_\beta} \tag{50b}$$

where $k_\alpha + k_\beta = k$ and $\max\{0, k - p_\beta, k - m + p_\beta\} \le k_\alpha \le \min\{p_\alpha, m - p_\alpha, k\}$. One of possible expressions for the star product of two wave functions is

$[\Psi * \Phi]_r$

$$= I^r + \sum_{k=0}^{r} \left\{ \sum_{k_\alpha} \sum_{\substack{J_\alpha \subset R_\alpha \\ I_\alpha \subset M - R_\alpha}}^{(k_\alpha)} \sum_{\substack{J_\beta \subset R_\beta \\ I_\beta \subset M - R_\beta}}^{(k_\beta)} e_{J_\alpha, J_\beta}^{I_\alpha, I_\beta} \sum_{k'=0}^{k} \sum_{k'_\alpha} \sum_{\substack{J'_\alpha \subset J_\alpha \\ I'_\alpha \subset I_\alpha}}^{(k'_\alpha)} \sum_{\substack{J'_\beta \subset J_\beta \\ I'_\beta \subset I_\beta}}^{(k'_\beta)} (-1)^{\varepsilon} x_{J'_\alpha, J'_\beta}^{I'_\alpha, I'_\beta} y_{J_\alpha - J'_\alpha, J_\beta - J'_\beta}^{I_\alpha - I'_\alpha, I_\beta - I'_\beta} \right\}$$
$$\tag{51}$$

where $k'_\alpha + k'_\beta = k'$, $\max\{0, k' - k_\beta\} \le k'_\alpha \le \min\{k', k_\alpha\}$, and

$$\varepsilon = \sum_{\sigma = \alpha, \beta} \left[|(J'_\sigma \cup I'_\sigma) \cap \Delta_{(J_\sigma \cup I_\sigma)}| + k'_\sigma \right] \tag{52}$$

Summation limits over k_α and k'_α require probably some comments. We have inequalities

$$0 \le k_\alpha \le p_\alpha$$
$$0 \le k_\alpha \le m - p_\alpha$$
$$0 \le k - k_\alpha \le p_\beta$$
$$0 \le k - k_\alpha \le m - p_\beta$$

and, consequently, $k_\alpha \ge \max\{0, k - p_\beta, k - m + p_\beta\}$, $k_\alpha \le \min\{k, p_\alpha, m - p_\alpha\}$. As for k'_α, we have

$$0 \le k'_\alpha \le k_\alpha$$
$$0 \le k' - k'_\alpha \le k_\beta$$

which means that $\max\{0, k' - k_\beta\} \le k'_\alpha \le \min\{k', k_\alpha\}$. Simple part of the star product in Eq. (51) corresponds to $k' = 0, k$ and is $x_{\emptyset, \emptyset}^{\emptyset, \emptyset} \Phi + \Psi y_{\emptyset, \emptyset}^{\emptyset, \emptyset}$.

The second version of formula for the star product is

$$[\Psi * \Phi]_r = I^r + \sum_{k=0}^{r} \sum_{k_\alpha} \sum_{\substack{J_\alpha \subset R_\alpha \\ I_\alpha \subset M - R_\alpha}}^{(k_\alpha)} \sum_{\substack{J_\beta \subset R_\beta \\ I_\beta \subset M - R_\beta}}^{(k_\beta)} x_{J_\alpha, J_\beta}^{I_\alpha, I_\beta}$$

$$\times \left[\sum_{k'=0}^{r-k} \sum_{k'_\alpha} \sum_{\substack{J'_\alpha \subset R_\alpha - J_\alpha \\ I'_\alpha \subset M - R_\alpha - I_\alpha}}^{(k'_\alpha)} \sum_{\substack{J'_\beta \subset R_\beta - J_\beta \\ I'_\beta \subset M - R_\beta - I_\beta}}^{(k'_\beta)} e_{J_\alpha \cup J'_\alpha, J_\beta \cup J'_\beta}^{I_\alpha \cup I'_\alpha, I_\beta \cup I'_\beta} (-1)^\varepsilon y_{J'_\alpha, J'_\beta}^{I'_\alpha, I'_\beta} \right] \quad (53)$$

$$\varepsilon = \sum_{\sigma = \alpha, \beta} |(J'_\sigma \cup I'_\sigma) \cap \Delta_{(J_\sigma \cup I_\sigma)}| \quad (54)$$

In the above equations r is the maximal excitation level used. For full (not quotient) product $r = \min\{p, 2m - p\}$. Note that simple contributions in the last expression correspond to $k = 0$ and $k' = 0$.

At present we are using the second expression for the star product modulo r because in our realization the corresponding algorithm works faster than that based on the first expression.

Any computer implementation of the star product requires algorithm for generation of subsets with fixed number of elements contained in a given index set. For this there exists a variety of methods which differ in subset orderings: lexical, Gray, revolving door, etc. Apart from generation itself, very important also is availability of the corresponding ranking and unranking functions.

After series of experiments we came to the conclusion that the revolving door algorithm is the best for our purpose. This algorithm and accompanying ranking and unranking functions are described in [18]. The corresponding codes are free and can be found at *The Stony Brook Algorithm Repository* [30].

For our current purpose unranking function is of no use, but ranking one is compulsory. Let us denote by $\text{rank}_R J$ the rank of J as a subset of R in revolving door ordering, and by $\text{rank}_{(R_\alpha, R_\beta)}(J_\alpha, J_\beta)$ the rank of a pair of subsets calculated as

$$\text{rank}_{(R_\alpha, R_\beta)}(J_\alpha, J_\beta) = \left(\text{rank}_{R_\alpha} J_\alpha - 1\right) \binom{p_\alpha}{k_\alpha} + \text{rank}_{R_\beta} J_\beta \quad (55)$$

Then for given $k, k_\alpha, J_\alpha, J_\beta, I_\alpha$, and I_β the position of the corresponding element in a row vector representing wave function (as well as its amplitude) is determined with the aid of the following mapping:

$$(k, k_\alpha, J_\alpha, J_\beta, I_\alpha, I_\beta) \mapsto \text{offset}(k, k_\alpha)$$

$$+ \left(\text{rank}_{(R_\alpha, R_\beta)}(J_\alpha, J_\beta) - 1\right) \binom{m - p_\alpha}{k_\alpha} \binom{m - p_\beta}{k_\beta}$$

$$+ \text{rank}_{(M - R_\alpha, M - R_\beta)}(I_\alpha, I_\beta) \quad (56)$$

Table 1 Timing of star product modulo r calculations (Intel Fortran, CPU Q9550@2.83 GHz, sequential mode)

Excitation level r	Dimension of the amplitude space	Time (s)
3	18,818	0.02
4	98,693	0.35
5	294,965	2.75
6	55,8809	13.04
7	755,081	38.49
8	834,956	74.62
9	851,956	103.10
10	853,702	115.27
11	853,774	117.95
12	853,775	118.23

and where the array of offset indices (filled only once at the beginning of calculation) is

$$\text{offset}(k, k_\alpha) = \sum_{k'=1}^{k-1} \sum_{k'_\alpha = \max\{0, k'-p_\beta, k'-m+p_\beta\}}^{\min\{k', p_\alpha, m-p_\alpha\}} \binom{p_\alpha}{k'_\alpha} \binom{m-p_\alpha}{k'_\alpha} \binom{p_\beta}{k'_\beta} \binom{m-p_\beta}{k'_\beta}$$

$$+ \sum_{k'_\alpha = \max\{0, k-p_\beta, k-m+p_\beta\}}^{k_\alpha - 1} \binom{p_\alpha}{k'_\alpha} \binom{m-p_\alpha}{k'_\alpha} \binom{p_\beta}{k'_\beta} \binom{m-p_\beta}{k'_\beta} \quad (57)$$

The computer code was written in FORTRAN 95 and was heavily tested. Example of time characteristics of the current computer implementation of the star product modulo r is given in Table 1.

7 Comparison of different polynomial parametrizations on concrete examples

Let us suppose that for a molecule under consideration orthonormal set of MOs is generated at the Hartree-Fock (HF) level of theory, active space is chosen, and full CI calculation of few low-lying electronic states is performed in this active space. Let Ψ_{CI} be one of the calculated wave functions. Our nearest aim is to compare this exact (*in a given active space*) wave function with its approximation by different polynomial functions for different excitation levels. To this end we first use GAMESS US program [31] (ALDET route) to generate coefficients of CI expansion over the determinant basis set. Then the maximal by absolute value CI coefficient is found and the corresponding determinant is taken as the reference one. The next step is to reorder CI coefficients in the ordering defined by the mapping (56) (in GAMESS the lexical ordering is accepted). Then the CI wave function is divided by the coefficient C_0 by the reference determinant and for a selected polynomial parametrization *the exact amplitude vector is determined*:

$$\tau_a^{\text{exact}} = P_a^{-1}(e_{\emptyset,\emptyset}^{\emptyset,\emptyset} + x) \tag{58}$$

where $x = \frac{1}{C_0}\Psi_{FCI} - e_{\emptyset,\emptyset}^{\emptyset,\emptyset}$. 'Exact' means that $P_a(\tau_a^{\text{exact}}) = \frac{1}{C_0}\Psi_{FCI}$. This amplitude vector depends on the parametrization used, therefore carries subscript a, and involves, in general, all possible excitations from the reference state.

Two questions may be posed:

(i) Suppose that the exact amplitude vector is truncated to the level r, and full expansion of the wave function $P_a(\tau)$ is calculated. The question is: At what excitation level the polynomial of exact but truncated amplitude becomes reasonably close to the CI function?

(ii) Suppose that the truncated amplitude vector is optimized to make $\|P_a(\tau) - \Psi_{CI}\|$ as small as possible (a kind of least square problem). The question is: In what cases optimization may essentially improve polynomial approximation of Ψ_{CI}? In detail the function

$$F(\tau) = \left[\sum_{R_\alpha, R_\beta} \left(\langle P_a(\tau)|R_\alpha, R_\beta \rangle - \langle \Psi_{CI}|R_\alpha, R_\beta \rangle \right)^2 \right]^{\frac{1}{2}} \tag{59}$$

should be minimized with respect to τ to get amplitude vector τ^* ensuring the best polynomial approximation of Ψ_{CI}.

Of quite a large number of performed calculations of atomic and molecular wave functions in different bases and with different active spaces we give here the results for only three molecular systems: (1) calculation of hypothetic ylide molecule $H_2C - NH - CHF$ ground state which is strongly correlated; (2) calculation of N_2O molecule ground state; (3) calculation of the first excited (triplet) state of boric acid molecule (its ground state is of no interest for us since it is practically non-correlated).

Comparison of quality for different polynomial appriximations of CI functions for the aforementioned molecules is depicted in Figs. (1)–(3) and presented in Tables (2)–(3).

In figures the descrete points on the abscissa axis correspond to the excitation levels (triple, quadruple, etc) whereas on the ordinate axis the values of $\|P_a(\tau) - \Psi_{CI}\|$ function are given. Directly in figures relevant information about basis sets used, dimensions of active spaces, and CI space dimensions may also be found.

From Figures and Tables it is seen that *all* polynomial parametrizations give equally good approximations of CI functions for ylide and boric acid starting from excitation levels 5 or 6. For lower excitation levels exponential parametrization is beyond comparison giving the best results. Behaviour of polynomial approximations in the course of amplitude optimization is of special interest. Such optimization may essentially improve wave function approximation for, say, the resolvent (Q polynomial) or the quadratic ($q_{\frac{1}{2}}$ polynomial) parametrizations. In the CI case the aforementioned optimization is of no meaning since the optimal truncated amplitude vector just coincides with the truncated part of the CI expansion divided by C_0. And it seems that the exponential parametrization inherits this property of truncated CI expansions. Namely, it possesses the following for the time being empirical but important property:
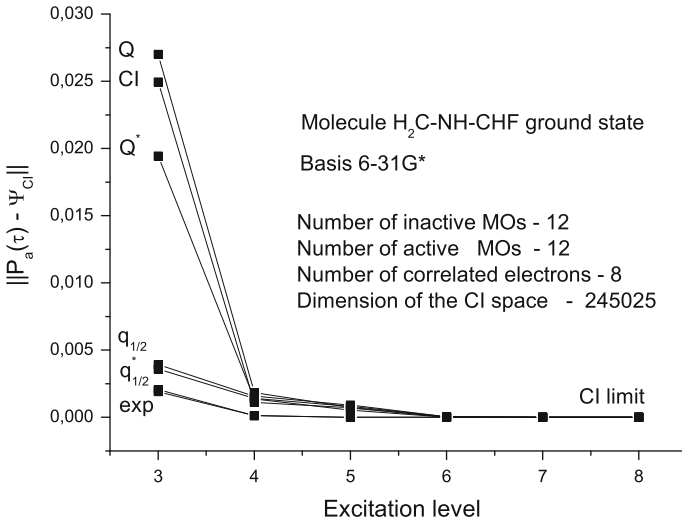
Fig. 1 Comparison of different polynomial approximations on example of the ground state of molecule H_2C-NH-CHF. Curves corresponding to optimized amplitudes carry additional label*
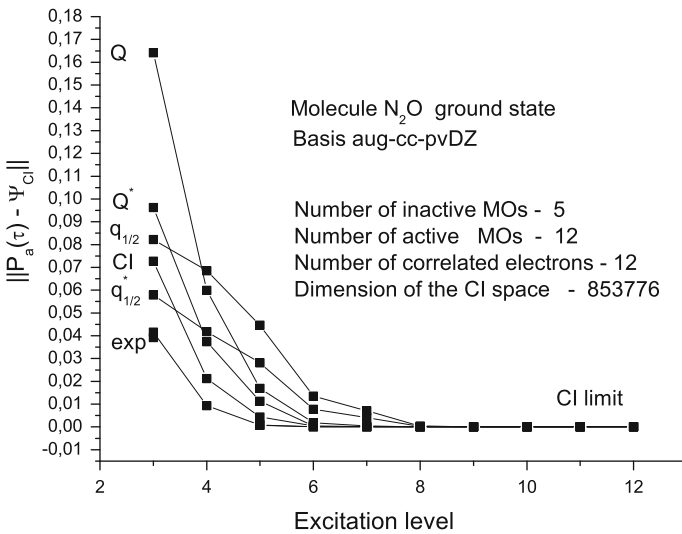

Fig. 2 Comparison of different polynomial approximations on example of the ground state of molecule N_2O. Curves corresponding to optimized amplitudes carry additional label*

For exponential parametrization the optimal amplitude vector involving excitations up to sufficiently high level r is a very good approximation to the exact amplitude vector truncated to the same excitation level. To put it differently, the solution of the least square problem for the truncated amplitude vector with high precision gives the trucated part of the exact amplitude vector.
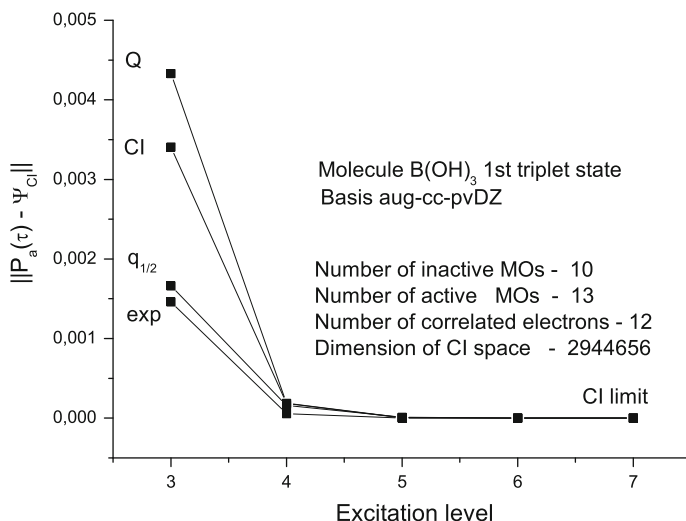
Fig. 3 Comparison of different polynomial approximations on example of the 1st triplet state of boric acid molecule

It is to be noted that, if the excitation level is reasonably high, quadratic parametrization gives, as a rule, approximation of wave functions close in its quality to the exponential parametrization. However, for low excitation levels the behaviour of such simple parametrization may be strange, unpredictable, and certainly system dependent as in the case of the nitrous oxide molecule (see Fig. 2).

And in conclusion to this section it is pertinent to mention that all parametrizations with excitation levels 1 and 2 in amplitude vector give poor approximations of wave functions as seen from Tables (2), (3). At the same time for relatively high excitation levels the use of strongly non-linear parametrizations (say, the exponential one) is hardly justified. Instead quadratic, or even linear parametrizations can be used with equal success.

8 Conclusion

This work completes the general algebraic theory of the finite dimensional electronic Fock spaces endowed with the star product. As the first application of the revealed algebraic structure a new approach to non-linear quantum chemistry methods was developed. Efficient computer implementation of the star product for the most general case made it possible to compare different polynomial approximations of many-electron wave functions for different excitations levels. Further generalizations embracing theories with MO optimization require essentially more complicated mathematical tools of modern differential geometry, in particular, theory of vector bundles. In this way it is possible to construct the theory including practically all existing wave function based variational methods of quantum chemistry.

Table 2 Comparison of different parametrizations: Ground state of molecule $H_2C - NH - CHF$

Polynomial $P_a(\tau)$	Excitation level	Dimension of the amplitude space	$\|P_a(\tau) - \Psi_{FCI}\|$	$\|P_a(\tau^*) - \Psi_{FCI}\|$
$\exp(\tau)$	1	64	0.420632E+00	0.417226E+00
	2	1,424	0.153643E-01	0.144873E-01
	3	12,624	0.207110E-02	0.191069E-02
	4	55,324	0.123119E-03	0.113253E-03
	5	135,068	0.114390E-04	0.114390E-04
	6	208,764	0.375204E-06	0.375204E-06
$Q(\tau)$	1	64	0.438430E+00	0.425482E+00
	2	1,424	0.550005E-01	0.405679E-01
	3	12,624	0.270095E-01	0.194293E-01
	4	55,324	0.183023E-02	0.135976E-02
	5	135,068	0.746502E-03	0.532138E-03
	6	208,764	0.118016E-04	0.888355E-05
$P_{CI}(\tau)$	1	64	0.406908E+00	
	2	1,424	0.396744E-01	
	3	12,624	0.249536E-01	
	4	55,324	0.112012E-02	
	5	135,068	0.709024E-03	
	6	208,764	0.872110E-05	
$q_{\frac{1}{2}}(\tau)$	1	64	0.420542E+00	0.417171E+00
	2	1,424	0.163069E-01	0.151996E-01
	3	12,624	0.390887E-02	0.359143E-02
	4	55,324	0.157044E-02	0.139820E-02
	5	135,068	0.917063E-03	0.815560E-03
	6	208,764	0.438127E-04	0.389069E-04

But in the framework of the purely algebraic approach described in this work there still exits one unsolved fundamental problem. This problem concerns the question of consistency between the star product and the standard Hermitean norm on the Fock space. In more rigorous terms, it is desirable to ascertain that the inequality $\|\Psi * \Phi\| \leq \|\Psi\|\|\Phi\|$ holds true for arbitrary p-electron wave functions when the number of MSOs is sufficiently large. If this statement is correct, then practically all the results described in this work can be easily reformulated for the infinite-dimensional Fock spaces and then the star product will become the property of quantum mechanics but not only of its finite dimensional model which is at present quantum chemistry.

Table 3 Comparison of different parametrizations: Ground state of molecule N_2O

Polynomial $P_a(\tau)$	Excitation level	Dimension of the amplitude space	$\|P_a(\tau) - \Psi_{FCI}\|$	$\|P_a(\tau^*) - \Psi_{FCI}\|$
$\exp(\tau)$	1	72	0.415883D+00	0.400344D+00
	2	1,818	0.110642D+00	0.106583D+00
	3	18,818	0.415729D-01	0.392551D-01
	4	98,693	0.938115D-02	0.887311D-02
	5	294,965	0.803279D-03	0.744422D-03
	6	558,809	0.450764D-04	0.412938D-04
$Q(\tau)$	1	72	0.628926D+00	0.4495243D+00
	2	1,818	0.347899D+00	0.1994256D+00
	3	18,818	0.164148D+00	0.9625347D-01
	4	98,693	0.599690D-01	0.3734982D-01
	5	294,965	0.168746D-01	0.1129635D-01
	6	558,809	0.191710D-02	0.1073262D-02
$P_{CI}(\tau)$	1	72	0.369100D+00	
	2	1,818	0.171212D+00	
	3	18,818	0.727427D-01	
	4	98,693	0.211776D-01	
	5	294,965	0.435432D-02	
	6	558,809	0.556137D-03	
$q_{\frac{1}{2}}(\tau)$	1	72	0.405992E+00	0.394752E+00
	2	1,818	0.119679E+00	0.110201E+00
	3	18,818	0.822454E-01	0.579319E-01
	4	98,693	0.685212E-01	0.418136E-01
	5	294,965	0.446974E-01	0.281541E-01
	6	558,809	0.135399E-01	0.771915E-02

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