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Theoretical
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Perspective

Perspective on "Group theoretical approach to the configuration interaction and perturbation theory calculations for atomic and molecular systems"

Paldus J (1974) J Chem Phys 61: 5321

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Abstract. This paper provides a "perspective" on the title paper of Paldus. The introduction of unitary groups into quantum chemistry has provided not only practical algorithms for many configuration-interaction-based methods still in current use, but has also provided a conceptual basis in quantum chemistry that is as important as the practical implementations.

Key words: Unitary groups – Configuration interaction

1 Introduction

A colleague recently remarked to me that a practising theoretical chemist who learned his "trade" in the 1990s has probably never heard of the unitary group approach (UGA) despite the fact that almost every quantum chemistry package in current use (excluding those devoted entirely to density functional computations) makes use, in some way, of the elegant UGA, first introduced into quantum chemistry in 1974 by Paldus. While the theory of continuous groups and the symmetric group was an essential part of the training of the theoretical chemist in the 1960s and 1970s, this subject is quite inaccessible to recently trained theoretical chemists. One of the reasons for this is that while the paper of Paldus gave a completely new insight into the configuration-interaction (CI) matrix-element problem, once this insight was achieved the applications and code development could proceed without the need to have a sound understanding of the basic mathematics (group theory) that led to this new insight in the first place.

Thus the purpose of this article is to try to describe the impact of Paldus' 1974 paper [1] (see also related accounts in Refs. [2, 3]) on the evolution of quantum chemistry at that time.The CI method itself has recently been reviewed by Shavitt [4] and the reader is referred to that paper for recent developments. We shall focus in this paper on the nature of the CI method as it existed in 1974 and the nature of the unitary group revolution introduced by Paldus that was subsequently turned into working algorithms by others [5–18] in the 10 years or so after its introduction.

2 The CI matrix-element problem 1957–1974

Let us begin our discussion with a simple discussion of the CI matrix-element problem. In the CI problem we seek the solution of the CI eigenvalue problem

$$\mathbf{HC} = \mathbf{EC} \ , \tag{1}$$

where

$$\mathbf{H} = \{\langle K|HL\rangle\} \tag{2}$$

is the representation matrix of the Hamiltonian in a basis of many-particle configuration state functions (CSF) which we denote as $\{|K\rangle\}$. The CSF, $\{|K\rangle\}$, can be chosen in a variety of ways (e.g. Slater determinants); however, in general, they are chosen to be eigenfunctions of S^2 and S_z. The central practical problem is the evaluation of the matrix $\langle K|HL\rangle$. The general formula for the matrix elements can be expressed as

$$\{\langle K|HL\rangle\} = \sum h_{ij}A_{ij}^{KL} + \frac{1}{2}\sum [ij|kl]B_{ijkl}^{KL} \ , \tag{3}$$

where h_{ij} and $[ij|kl]$ are the usual one- and two-electron repulsion integrals (in charge-cloud notation). The A_{ij}^{KL} and B_{ijkl}^{KL} are numerical "vector-coupling" coefficients that depend on the nature of $|K\rangle$ and $|L\rangle$. The preceding discussion hides a problem that was the most important one in 1974. The symbol $|K\rangle$ means an orbital string (of orbitals occupied in the CSF); however, it also stands for a sequence number or index. The central problem was establishing a unique one-to-one correspondence between the two.

Equation (3) can be read in two ways. On the one hand, given $|K\rangle$ and $|L\rangle$, it gives a prescription for forming a specific matrix element $\langle K|HL\rangle$ by providing a list of integral indices ij and $ijkl$ corresponding to nonzero contributions or "weights", A_{ij}^{KL} and B_{ijkl}^{KL}, for the one- and two-electron integrals that contribute to a given matrix element. This approach is the so-called matrix-element-driven CI method that was in use in 1974 in the Boys–Reeves bonded-function CI code [19] of the Polyatom program. However, Eq. (3) can be read the other way around. One can focus on an integral $[ij|kl]$. Then Eq. (3) provides a list of matrix element labels K, L to which that integral contributes. This is the direct CI approach introduced by Roos [20, 21] in 1972. In this approach, one can process the integrals in the CI eigenvalue iterations without the need to explicitly assemble the matrix $\mathbf{H}$. This direct CI approach is used in all CI-based methods today; however, Roos' method was originally formulated for the case where the self-consistent-held (SCF) result was a good starting point and the CI he used was built from all single and double replacements of the SCF orbitals. In this case the A_{ij}^{KL} and B_{ijkl}^{KL} are simple and can be derived using simple rules (based on the Slater formalism) found in any textbook on quantum chemistry.

As just pointed out, Roos' method was efficient but not general. One needed the methodology to carry out both full CI (all possible arrangements of electrons in the available orbitals) and a multireference CI (all possible single and double replacements from several reference configurations). Roos' method was only for single-reference CI. In the full CI and in the multireference CI case, not only does the configuration list become large, but also the indexing of the configurations becomes a major problem. For the indexing of the configurations, one needs an algorithm to associate a given string of occupied orbitals and the associated spin coupling, with a unique index K in the list of CI configurations. In the early 1970s there was no general solution to the CI indexing problem. One simply generated a list of configurations in some ad hoc fashion and wrote the information to a file. (In the Boys–Reeves CI program that was implemented in the Polyatom program in the late 1960s, the input to the program was just orbital strings that were punched on cards. The program then generated all possible spin couplings, so-called canonical sets, for each orbital pattern). This configuration-list file was then processed (comparing configurations two at a time) to generate the A_{ij}^{KL} and B_{ijkl}^{KL} which were written to a so-called symbolic matrix-element file. This file was then merged with the numerical values of the one and two integrals in the CI eigenvalue iterations. (In the Polyatom program of the 1960s this file filled several 2400-ft magnetic tapes for a CI with a mere 2000 configurations). Thus, this symbolic matrix-element file became unmanageably large very quickly and this proved to be an insurmountable problem until the introduction of UGA methods and direct CI concepts. Further, the computation of the symbolic matrix elements was so costly that the possibility of computing matrix elements "on the fly" was out of the question. Note that every pair of configurations needed to be examined to generate the symbolic matrix elements. There was no way to tell a priori which matrix elements would be zero.

Thus the development of general CI-based methods required the solution of two major problems:

1. A genealogical or hierarchical method of generating or indexing the configuration list was essential. What was required was an algorithm that established a one-to-one correspondence between a configuration index (K) in a hierarchically ordered list and all the orbital and spin-coupling information about that configuration.
2. A fast and efficient method was required for generating the A_{ij}^{KL} and B_{ijkl}^{KL} that could be used "on the fly" so that the symbolic matrix elements did not have to be stored in a symbolic matrix-element file.

As we shall now discuss, the UGA introduced by Paldus solves both these problems.

3 The essential elements of UGA [1–3]

In second quantization, the numerical "vector-coupling" coefficients (the A_{ij}^{KL} and B_{ijkl}^{KL}) appear as matrix elements of creation and annihilation operators $\mathbf{X}_{i\sigma}^{\dagger}$ and $\mathbf{X}_{j\sigma}$. The operator $\mathbf{X}_{i\sigma}^{\dagger}$ creates an electron in an orthonormal spin orbital $|i\sigma\rangle$, where $|i\sigma\rangle = |i\rangle|\sigma\rangle$, and $\sigma = \alpha$ or β. Similarly, operator $\mathbf{X}_{i\sigma}$ destroys an electron in the orthonormal spin orbital $|i\sigma\rangle$. In quantum chemistry problems in which the number of particles is conserved, the $\mathbf{X}_{i\sigma}^{\dagger}$ and $\mathbf{X}_{j\sigma}$ will always occur in pairs. The role of these operators is easily illustrated by showing their operation on a specific type of CSF, namely a Slater determinant. Thus, as an example, for the determinant

$$|\ldots\ldots i_\alpha\, j_\alpha \ldots\ldots k_\beta l_\beta \ldots\ldots|$$

we have simply

$$\mathbf{X}_{m\alpha}^{\dagger}\,\mathbf{X}_{i\alpha}|\ldots\ldots i_\alpha j_\alpha \ldots\ldots k_\beta l_\beta \ldots\ldots| = |\ldots\ldots m_\alpha j_\alpha \ldots\ldots k_\beta l_\beta \ldots\ldots|\ . \tag{4}$$

A good pedagogical discussion can be found in the book by Matsen and Pauncz [22].

In this "second quantized" formalism Eq. (3) becomes

$$\langle K|HL\rangle = \sum h_{ij}\left\langle K\middle|\sum_{\sigma}\mathbf{X}_{i\sigma}^{\dagger}\mathbf{X}_{j\sigma}L\right\rangle + \sum [ij|kl]\left\langle K\middle|\sum_{\sigma\gamma}\mathbf{X}_{i\sigma}^{\dagger}\mathbf{X}_{k\gamma}^{\dagger}\mathbf{X}_{l\gamma}\mathbf{X}_{j\sigma}L\right\rangle\ . \tag{5}$$

Thus we can write

$$A_{ij}^{KL} = \left\langle K\middle|\sum_{\sigma}\mathbf{X}_{i\sigma}^{\dagger}\mathbf{X}_{j\sigma}L\right\rangle \tag{6}$$

and

$$B_{ijkl}^{KL} = \left\langle K\middle|\sum_{\sigma\gamma}\mathbf{X}_{i\sigma}^{\dagger}\mathbf{X}_{k\gamma}^{\dagger}\mathbf{X}_{l\gamma}\mathbf{X}_{j\sigma}L\right\rangle\ , \tag{7}$$

where the summations over σ and γ are over spin.

For the reader who is encountering second quantization for the first time, one can observe that application of the definition of Eq. (4) for CSF built from Slater determinants in the context of (Eq. 6) just reduces to the usual rules for matrix elements between determinants if K and L are determinants; however the definitions of Eqs. (6) and (7) remain true irrespective of the nature of the CSF (and become very powerful when the CSF are chosen as spin eigenfunctions).

Since the $\mathbf{X}_{i\sigma}^{\dagger}$ and $\mathbf{X}_{j\sigma}$ always occur in pairs in Eqs. (6) and (7) it becomes convenient to define a "generator"

$$E_{ij} = \sum_{\sigma} \mathbf{X}_{i\sigma}^{\dagger}\mathbf{X}_{j\sigma} \ . \tag{8}$$

The vector-coupling coefficients now take the form

$$A_{ij}^{KL} = \langle K|E_{ij}L\rangle \tag{9}$$

and

$$B_{ijkl}^{KL} = \langle K|\left(E_{ij}E_{kl} - \delta_{jk}E_{li}\right)L\rangle \ . \tag{10}$$

It now remains to make the connection with unitary groups.

The unitary group $U(n)$ is the group of all $n \times n$ unitary matrices representing unitary transformations of the orthonormal orbitals $\{|i\rangle\}$. It is possible to show that the operators in Eq. (8) satisfy the commutation relations of generators of the unitary group $U(n)$.

$$\left[E_{ij}, E_{kl}\right] = \delta_{jk}E_{il} - \delta_{li}E_{kj} \ , \tag{11}$$

where the [ ] is the commutator i.e. $[A,B] = AB - BA$. Because of this fact, the matrix elements in Eq. (9) must be nothing other than group theoretical quantities (i.e. completely independent of the CI formalism). This point is important because the set of CSF remains implicit rather than explicit. There is no need to expand the CSF as linear combinations of Slater determinants. (Of course, the same fact is true for the bonded function approach of Boys and Reeves [13]). The recognition of this feature, in Paldus' 1974 paper, provides the solution of both problems in CI: the efficient evaluation of matrix elements and a genealogical classification for the CI basis functions. We now briefly discuss both points.

The completely general formulation of the representations of the unitary group was known to Paldus from the original work of Gelfand and Tsetlin [23]. Paldus' contribution was to recognise that the Gelfand and Tsetlin formalism becomes very simple for the CI problem in electronic structure theory and in his paper he presents a purely algebraic description that requires no prerequisite understanding of the details of the representation theory of continuous groups.

The basis for the classification and canonical ordering of CSF encountered in the CI method is chains of possible subgroups. When an irreducible representation (irrep) of a group is restricted to a subgroup the representation splits into a direct sum of irrep of the subgroup. If this subduction process is multiplicity-free (i.e. a given irrep of the subgroup occurs at most once in this process) and the last group in the chain is Abelian (and thus has only one-dimensional irreps) then the chain of subgroups and irrep labels provides a unique label for the state of interest. The reader will be familiar with this process, for example, in the classification of the $l = 1$ orbital-momentum states in $O(3)$ (L^2) and $O(2)$ (l_z). For $U(n)$ this subgroup chain is very simple

$$U(n) \supset U(n-1) \supset U(n-2) \bullet\bullet\bullet\, U(1) \ . \tag{12}$$

The "labels" for the CSF basis functions can thus be written as a triangular Gelfand tableau

$$\begin{bmatrix} m_{1n} & m_{2n} & \bullet\bullet\bullet\bullet\bullet\bullet\bullet & m_{nn} \\ \quad m_{1n-1} & m_{2n-1} & & \\ \quad\bullet\ \bullet & & & \\ & & & \\ & m_{11} & & \end{bmatrix} \ . \tag{13}$$

Each row of the tableau gives the irrep labels for $U(n)$, $U(n-1)$ ...etc. The hierarchical ordering comes from the "betweenness conditions". The integers in any row must lie between those of the previous row. For the electronic structure problem the integers m_{im} can have only three values: 2, 1 or 0. Consequently, as Paldus discovered, each row of the Gelfand tableau could be denoted by

$$\Gamma_i = 2^{a_i}1^{b_i}0^{c_i} \ , \tag{14}$$

where a_i counts the number of 2s in row i, etc. The integers a_i, b_i and c_i thus classify the CSF in $U(i)$ and have the following simple relationship.

$$n = a + b + c \tag{15}$$

$$a = N/2 - S \tag{16}$$

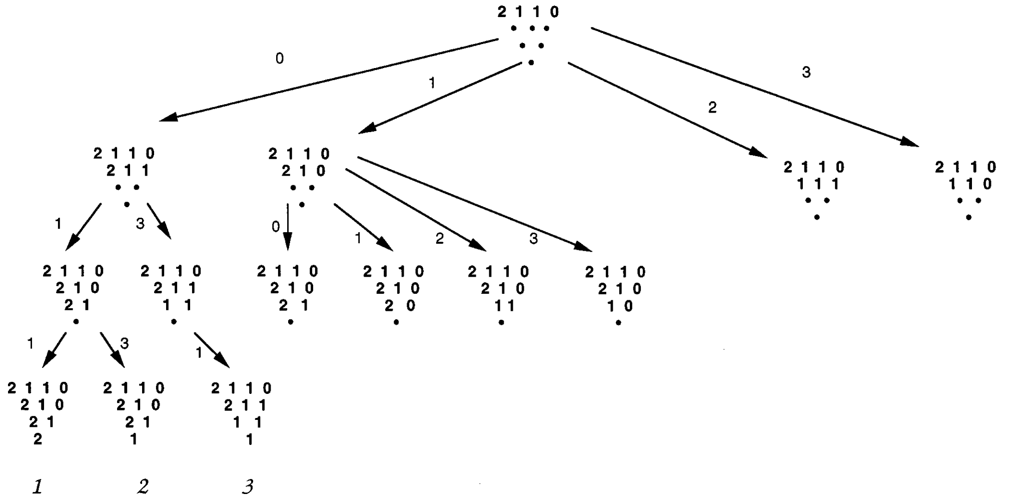
$$b = 2S \ , \tag{17}$$

where N is the number of electrons, n is the number orbitals and S is the spin.

Then one has the remarkable feature that makes the $U(n)$ method so powerful for electronic structure problems. Because of the restriction of the entries in the Gelfand tableau to 2, 1 or 0 there are only four ways of adding a lower row to a tableau and still satisfy the betweenness conditions. This leads to the genealogical representation (labelled by possible steps 0, 1, 2 or 3) of the CSF basis shown (in part) in Eq. (18) for $U(4)$ (four orbitals and four electrons) with a full CI with triplet spin multiplicity ($\Gamma_n = 2^1 1^2 0^1$).

Remarkably the sequence of step vectors [e.g. (0 1 1) for basis vector 1 or (0 3 1) for basis vector 3] in Eq. (18) is enough to specify all the information that is required about a CSF and to establish an algorithm for the implicit representation of the basis.

We turn briefly to the second contribution in Paldus' paper: the computation of the matrix elements themselves. Paldus derived the formulae (from the complicated formulae of Gelfand and Tsetlin [23]) for the so-called elementary generators $E_{i,i+1}$. These were both simple and, more importantly, gave only the nonzero matrix elements directly using only the step vectors as "inputs". Paldus states that the general program



(18)

required only 400 "cards". The remaining matrix elements could be found from the commutation relationships

$$[E_{ij}, E_{jl}] = E_{il} \ . \tag{19}$$

In addition, the two-particle matrix elements could be obtained from

$$B^{KL}_{ijkl} = \sum_M \langle K|E_{ij}M\rangle\langle M|E_{kl}L\rangle - \delta_{jk}\langle K|E_{li}L\rangle \ , \tag{20}$$

where the summation over M was over all the basis states. In his 1974 paper, Paldus did not put these two ideas together into a working algorithm. Rather both ideas formed the basis of the practical approach that Shavitt [5] was shortly to follow.

Thus, in Paldus 1974 paper one has, in principle, the method for the hierarchical basis function generation and the computation of the matrix elements themselves. The evolution of the method to become a practical tool in quantum chemistry then proceeded rapidly. We now very briefly bring the article to its conclusion with a brief mention of these key developments by Shavitt and by Siegbahn.

The development of UGA post 1974

Efficient subsequent general CI algorithms were based upon the subsequent graphical implementation of UGA by Shavitt [5, 6]. Shavitt derived a graphical representation [5] for the genealogical representation illustrated in Eq. (18) and showed that it could be represented efficiently on a computer via a "distinct row table". He also observed that the nonzero matrix elements corresponded to closed loops on his graph. The importance of this loop structure comes from the fact that many matrix elements have the same matrix-element loop but differed only in the "upper" and "lower" walks on the graph. This observation means that the numerical value of the matrix-element "loop" needed only to be computed once and its contribution to all the matrix elements to which it contributed could be evaluated immediately by "following" the upper and lower walks. However, the most important breakthrough came when Shavitt recognised [6] that the evaluation of the matrix elements in the loop could be formulated in terms of sums of products of "segments" within these loops for each orbital level on the graph. This eliminated the last bottleneck which arises because of the sum over M in Eq. (20). Thus a CI code could be developed that was "loop" or "shape" driven [18], where all the matrix elements could be evaluated "on the fly" without storing any formula tape.

However, while loop-driven methods provide a good approach to full CI, for multireference CI, these methods are too general. Thus the final chapter in the UGA story comes from the work of Siegbahn [7–10]. Siegbahn noticed that in multireference CI the matrix-element segments that occurred in levels in the virtual orbital space were particularly simple. He showed that one can confine the detailed analysis required for matrix formula determination to the levels that correspond to reference space orbitals. The contribution from the levels that correspond to virtual levels, which take the same form in all calculations, can be built into the structure of the computer program rather than being treated in a general way.

Thus, at the end of the story, most of the complexity of the general matrix-element problem for CI goes away. The general matrix-element problem remains only for the reference space part of multireference CI; however, Siegbahn would certainly never have discovered this fact without the general formalism introduced by Paldus and its graphical realisation by Shavitt. It is worth noting that Shavitt's graphical approach was carried out heuristically. He did not need to understand the (beautiful) theory of continuous groups. Rather it is the structure of the CI problem that emerges from Paldus work that was the important breakthrough.

5 Conclusion

In this perspective we have focused on the nature of the CI method as it existed in 1974 and on the nature of the unitary group revolution introduced by Paldus. This method was subsequently turned into working algorithms by others [5–18] in the 10 years or so after its introduction. Of the developments post 1974 we have only mentioned the work of Shavitt and Siegbahn because they introduced the first steps that were needed to make the method work in practice. The reader is referred to Refs. [5–18] to trace the immediately subsequent developments in more detail. Of course, there has been much development of the subject since the early 1980s and the interested reader might start by looking at Ref. 24.

The lasting importance of Paldus' 1974 paper stems from the fact that it introduced a new way of thinking into quantum chemistry problems related to the CI method.

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