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Computer-Aided Construction of Symmetry Adapted Wave Functions and Matrix Elements

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ABSTRACT

A LISP 1.5 program is described which calculates the Matsen pair-operators and the Chi-operators. The Matsen pair-operators project symmetry adapted wave functions out of a spin-free primitive function. From the Chi-operators the matrix elements between these symmetry adapted wave functions may be obtained.

I. INTRODUCTION

The basic problem of quantum chemistry is the calculation of many-electron wave functions for atoms and molecules given a Hamiltonian H. Neglecting nuclear motion, relativistic effects and spin interactions H includes only the kinetic energy for the electrons and the electrostatic interactions among the electrons and nuclei. This Hamiltonian is invariant under all permutations of the electrons, i.e. under the operations of the symmetric group S_n (n being the number of electrons), and commutes with all spin operators, including S^2 and S_z, the operators of the total spin. The symmetry condition on the wave function resulting from the invariance of H under the symmetric group S_n is formulated in the Pauli principle. The Pauli principle states that for any permutation of the spatial-spin coordinates the wave function must behave in an antisymmetric manner. From the fact that H commutes with the operators of the total spin follows that the wave function must be an eigenfunction of S^2 and S_z. Hence, one is faced with the problem of constructing many-electron wave functions that simultaneously are eigenfunctions of S^2 and S_z and satisfy the antisymmetry principle.

A general method for obtaining antisymmetric many-electron wave functions being eigenfunctions of S^2 has been developed by Goddard [1]. Using Young's orthogonal units [2], Goddard constructs an operator G_i^{α} such that $G_i^{\alpha}\psi$ has the desired spin and antisymmetry properties, if ψ is any function of the spatial-spin coordinates of n electrons. Although the wave functions constructed by the

GI-method are equivalent to those obtained using the earlier Yamanushi [3]-Kotani [4] method[1] the GI-method has the advantage of the close relationship to the Young tableaux. Clearly, Hartree–Fock and extended Hartree–Fock wave functions are special cases of the Yamanushi–Kotani (resp. GI) wave functions [5].

Since the spin plays no role in the dynamics of a system described by a spin-free Hamiltonian one may eliminate the spin from the wave mechanical description [6]. The eigenfunctions of S^2 satisfying the antisymmetry principle are replaced by spin-free functions with irreducible symmetry under the symmetric group S_n. For every spin-free observable these spin-free functions are equivalent to the antisymmetric space-spin functions [6], [7]. To project a spin-free n-electron wave function ϕ into the α-th permutation state Matsen [6] uses the "pair operators", κ_i^{α}, described in the next section. Corresponding to the several independent spin-coupling schemes giving eigenfunctions of S^2 there are f^{α} linearly independent spin-free functions $\kappa_i^{\alpha}\phi$, $i = 1 \cdots f^{\alpha}$, forming a basis for spin-free quantum chemistry. In a series of papers, [8]–[12], Matsen and his coworkers have shown this spin-free method to be a very clear and operative concept.

II. Pair and Chi-Operators

The pair operators κ_i^{α} projecting a spin-free n-electron primitive functions into the αth permutation state are elements of the invariant subalgebra A^{α} of the algebra on the symmetric group S_n. α denotes a partition of n characterizing the permutation state. From the antisymmetry principle and the fact that there are only two spin states for an electron follows that the only states allowed are those with

$$\alpha = [2^p, 1^{n-2p}], \qquad 0 \leqslant p \leqslant n/2. \tag{1}$$

Matsen's pair number p is directly related to the total spin S of the n-electron system,

$$p = n/2 - S \tag{2}$$

Eqs. (1) and (2) constitute a one-to-one correspondence between the permutation states characterized by $\alpha = [2^p, 1^{n-2p}]$ and the spin states in the conventional formulation of quantum chemistry.

[1] There are different spellings of the name Yamanushi in use. The french spelling Yamanouchi ist mostly found in literature. However, we chose the official Japanese Hepburn–Romaji transcription.

To obtain the pair operators κ_i^α we construct the normal tableau T_1^α associated with the partition α of Eq. (1):

$$T_1^\alpha = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline \vdots & \vdots \\ \hline 2p-1 & 2p \\ \hline 2p+1 & \\ \hline \vdots & \\ \hline n & \\ \hline \end{array}$$

The pair operator κ_1^α is the algebra element

$$\kappa_1^\alpha = Q_1^\alpha P_1^\alpha \tag{3}$$

Here P_1^α is the sum of all elements of $\mathbf{P}_1^\alpha$ and Q_1^α is the sum of all elements of $\mathbf{Q}_1^\alpha$; $\mathbf{P}_1^\alpha$ denoting the product of the symmetric groups of the rows of the tableau T_1^α and $\mathbf{Q}_1^\alpha$ the product of the negative symmetric groups of the columns of T_1^α. (The negative symmetric group is obtained by the substitution $\pi \to \zeta(\pi)\pi$ in the symmetric group.) The pair operators κ_i^α, $i = 1 \cdots f^\alpha$, are defined by the formula [6]

$$\kappa_i^\alpha = \zeta(\sigma_{1i})\, Q_1^\alpha P_1^\alpha \sigma_{1i} \tag{4}$$

where $\zeta(\pi)$ is the parity of the permutation π, i.e. is $+1$ if π is an even permutation and -1 if it is odd. σ_{1i}, $i = 1 \cdots f^\alpha$, are the permutations changing the standard tableaux T_i^α, $i = 1 \cdots f^\alpha$, into the normal tableau T_1^α.[2] The standard tableaux are those tableaux for which the integers are arranged in ascending order along the rows and down the columns.

The algebra elements (4) may be used to obtain a set of f^α linear independent functions ϕ_i^α lying in the αth permutation state,

$$\phi_i^\alpha = \kappa_i^\alpha \phi, \qquad i = 1 \cdots f^\alpha. \tag{5}$$

[2] Matsen uses the canonical tableaux constructed from the canonical pair diagrams [6].

ϕ is a spin-free n-electron primitive wave function. Now with the functions defined in Eq. (5) a matrix of the system Hamiltonian is constructed. An eigenvalue problem results. The rth eigenfunction in the αth permutation state is

$$\varphi_r{}^{\alpha} = \sum_{i=1}^{f^{\alpha}} c_{ir}^{\alpha} \phi_i{}^{\alpha} \tag{6}$$

In solving the eigenvalue problem the matrix elements $\langle \phi_i{}^{\alpha} \mid H \mid \phi_k{}^{\alpha} \rangle$ have to be evaluated. Substitution from Eq. (5) yields

$$\langle \phi_i{}^{\alpha} \mid H \mid \phi_k{}^{\alpha} \rangle = \langle \kappa_i{}^{\alpha} \phi \mid H \mid \kappa_k{}^{\alpha} \phi \rangle \tag{7}$$

By means of the quantum mechanical "turn over rule"

$$\langle \psi_1 \mid F \psi_2 \rangle = \langle F^{+} \psi_1 \mid F_2 \rangle \tag{8}$$

and the invariance of the Hamiltonian under the symmetric group we get

$$\langle \phi_i{}^{\alpha} \mid H \mid \phi_k{}^{\alpha} \rangle = \langle \kappa_k^{\alpha +} \kappa_i{}^{\alpha} \phi \mid H \mid \phi \rangle. \tag{9}$$

Since

$$\kappa_k^{\alpha +} = \zeta(\sigma_{k1})\, \sigma_{k1} P_1{}^{\alpha} Q_1{}^{\alpha} \tag{10}$$

we obtain the following expression for the algebra element $\kappa_k^{\alpha +} \kappa_i{}^{\alpha}$:

$$\kappa_k^{\alpha +} \kappa_i{}^{\alpha} = \zeta(\sigma_{k1})\, \sigma_{k1} P_1{}^{\alpha} Q_1{}^{\alpha} Q_1{}^{\alpha} P_1{}^{\alpha} \sigma_{1i} \zeta(\sigma_{1i}). \tag{11}$$

$Q_1{}^{\alpha}$ is essentially idempotent, viz.

$$Q_1{}^{\alpha} Q_1{}^{\alpha} = m^{\alpha} Q_1{}^{\alpha}, \qquad m^{\alpha} = (n-p)!\, p!, \tag{12}$$

hence,

$$\kappa_k^{\alpha +} \kappa_i{}^{\alpha} = m^{\alpha} X_{ik}^{\alpha} \tag{13}$$

$$X_{ik}^{\alpha} = \zeta(\sigma_{ik})\, \sigma_{k1} P_1{}^{\alpha} Q_1{}^{\alpha} P_1{}^{\alpha} \sigma_{1i} \tag{14}$$

Using the Chi-operators X_{ik}^{α} defined by Eq. (14) the matrix element $\langle \phi_i{}^{\alpha} \mid H \mid \phi_k{}^{\alpha} \rangle$ may be written in the following form

$$\begin{aligned} \langle \phi_i{}^{\alpha} \mid H \mid \phi_k{}^{\alpha} \rangle &= m^{\alpha} \langle X_{ik}^{\alpha} \phi \mid H \mid \phi \rangle \\ &= m^{\alpha} \sum_{\pi} \lambda_{ik}^{\alpha}(\pi) \langle \pi \phi \mid H \mid \phi \rangle \end{aligned} \tag{15}$$

The $\lambda_{ik}^{\alpha}(\pi)$ are the numerical coefficients of the permutations π in the algebra element X_{ik}^{α}. If the canonical tableaux [6] are chosen instead of the standard

tableaux then, except for a normalization factor, the numerical coefficients $\lambda^{\alpha}_{ik}(\pi^{-1})$ are identical to the familiar Pauling numbers π^{α}_{ik}, and the Hermitian adjoints of the Chi-operators $(X^{\alpha}_{ik})^{+}$ are identical to the Z^{α}_{ik} operators of Matsen, Cantu, and Poshusta [9].

III. The Program

Because algebra elements are essentially symbol strings whose length varies over a wide range in the course of computation and therefore demand for an easy mechanism to insert or delete a permutation π with its associated numerical factor λ the problem is beyond the capabilities of a usual numerical computing language as FORTRAN or ALGOL. Hence, to program the manipulation of algebra elements a list processing language as LISP ([13], [14]) or a similar language [15] is appropriate. As a first step list representations[3] of the algebra elements on the symmetric group and of Young tableaux must be defined. For permutations the usual cycle representation

$$\pi = (\text{cycle}_1\ \text{cycle}_2 \cdots \text{cycle}_i \cdots \text{cycle}_s), \qquad s \geqslant 0,$$

with

$$\text{cycle}_i = (m_{i1}\ m_{i2} \cdots m_{ij} \cdots m_{it}), \qquad t > 1,$$

may be used, m_{ij} being natural numbers. Cycles consisting of one number only (i.e. an element remaining unchanged under permutation) will be omitted from the list representation of π. Given the number n of objects (electrons) to be permuted, each natural number $m_{ij} \leqslant n$ can appear at most in one of the sublists representing cycles in the list describing the permutation π. Clearly the identity permutation ϵ is represented by an empty list ( ).

To represent an algebra element $q = \sum \lambda(\pi)\pi$ the numerical factor $\lambda(\pi)$ may be conveniently included in the list representation of a permutation giving a list

$$\lambda\pi = (\lambda\ \text{cycle}_1 \cdots \text{cycle}_2 \cdots \text{cycle}_s).^{4}$$

Finally an algebra element can be written as a list of its constituent permutations including the numerical factors, viz.

$$q = (\lambda\pi_1\ \lambda\pi_2 \cdots \lambda\pi_k \cdots \lambda\pi_v).$$

[3] A "list" to be manipulated by a list processing language is a string of numerical or character objects (usually called "atoms") enclosed in parentheses, e.g. $(A\ B\ C)$. Lists may also contain sublists, e.g. $((A\ B)(C\ D)\ E)$. Besides of lists the "dotted pair" is the second type of structure which can be manipulated by the LISP system. A dotted pair is written $(A.B)$. The objects left and right from the dot may be atoms, lists or again dotted pairs.

[4] In LISP notation the following relations hold:

$$\lambda = \text{car}[\lambda\pi], \qquad \pi = \text{cdr}[\lambda\pi], \qquad \lambda\pi = \text{cons}[\lambda; \pi].$$

Permutations having the numerical factor $\lambda = 0$ need not actually appear in the list, hence the number v of permutations $\lambda\pi_k$ in the list representation of an algebra element is in nearly all cases of practical interest smaller than $n!$.

To allow for automatic simplification of algebra elements arising in the progress of calculation ordering conventions for numbers in cycles, cycles in permutations and permutations in algebra elements are indispensable. These conventions are largely arbitrary. We choose the following ones:

1) Every cycle will be written with its smallest constituent integer being the first one.
2) In a permutation the cycles are ordered with increasing first numbers.
3) To each permutation a "structure list"

   structure = ((number of cycles) (length of first cycle)
   (length of second cycle) ⋯
   (length of last cycle))

   is attached. The permutations in an algebra element can then be ordered according to increasing first, second, etc., numbers in their respective structure lists.
4) Permutations with equal structure lists are ordered according to increasing first, second, etc., numbers in their list representations (π = cdr [$\lambda\pi$]) irrespective of the parentheses breaking them down in sublists (cycles). With these conventions it is not difficult to write LISP routines to multiply permutations and algebra elements.

The second main task is the construction of all standard tableaux to given electron number n and pair number p. Since the tableaux under study have at most two columns they may be represented by "dotted pairs" of lists giving the first and second column, respectively, e.g. ((1 3 5). (2 4)) for the "normal tableau"

$$T_1 = \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline 5 \\ \cline{1-1}\end{array}\ .$$

A more elegant list representation for standard tableaux is the "Yamanushi symbol"

$$r = (z_1\ z_2 \cdots z_n).$$

Here the integer z_1 denotes the row of the associated standard tableau containing

the integer 1, z_2 the row containing the integer 2, and so on. The Yamanushi symbol associated to the normal tableau T_1 given above is

$$r_1 = (1\ 1\ 2\ 2\ 3).$$

To describe a standard tableau of at most two columns the numbers in the Yamanushi symbol have to comply with the following rules:

1) For n electrons and p pairs each integer $m \leqslant p$ will be found two times, each integer m with $p < m \leqslant n - p$ once in the Yamanushi symbol.
2) The first appearance of an integer m in the Yamanushi symbol (read from left to right) cannot take place if not all smaller integers are already represented at least once, the second appearance not earlier than all smaller ones are already contained twice in the symbol.

On the other hand, all symbols fulfilling these demands are acceptable standard tableaux. This fact is used in a LISP routine which constructs a list of all standard tableaux to given n and p.

If all standard tableaux are obtained, it is easy to program the calculation of the column antisymmetrizer Q_1 and the row symmetrizer P_1 for the normal tableau as well as the permutations σ_{1k} which transform a tableau T_k into the corresponding normal tableau T_1. The Matsen pair-operators K_k and the Chi-operators X_{ik} are then obtained according to Eqs. (4) and (14) using the multiplication routine for algebra elements.

Because the list representation of algebra elements is difficult to read, especially in the case of lengthy expressions, an output routine should be provided which prints the algebra elements in a more readable format. An example for the final output obtained in the rather trivial case of $n = 3$, $p = 1$ is given in the appendix. The indices of the Chi-operators denote the respective standard tableaux. Permutations are written as cycles, the identity permutation is printed as the letter E. The numerical factors λ are given only if they are different from unity.

A full listing of the program written in the LISP 1.5-version distributed by SHARE for the IBM 7090/94 computer may be obtained from the authors [16].

IV. Conclusions

The object of this investigation was to study the use of a nonnumerical language for the mechanized construction of symmetry adapted wave functions and of the pertaining matrix elements of the Hamiltonian.

The LISP 1.5-program developed calculates for given electron number n and pair number p the Matsen pair-operators, which project wave functions of the right

symmetry out of a primitive, and Chi-operators X_{ik} from which the matrix elements may be obtained.

As usual for structure oriented computing the capacity of the core memory (rather than time restrictions as in most numerical computing) limits the complexity of the problems which can be processed. Depending on p the present program fails between $n = 6$ (group order $n! = 720$) and $n = 7$ (group order $n! = 5040$). Since each list representing a permutation needs on an average approximately n memory cells, this limit for the performance of the program was to be expected.

However, this relatively high expenditure of memory space to store a single permutation in list form cannot be called economical. Hence it seemed advantageous to build a special list processor to handle algebra elements in a more economical way. An experimental version of it will be described in a following paper.

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APPENDIX

Typical output giving the Matsen-pair-operators K_k and the Chi-operators X_{ik} in the simple case of $n = 3$ electrons having a total spin $S = 1/2$.

```
N = 3  ELECTRONS

P = 1  PAIRS

2  STANDARD TABLEAUX


STANDARD TABLEAU 1  = (1 1 2)

MATSEN OPERATOR ...

K =

 + E + (1 2) - (1 3) - (1 2 3)

STANDARD TABLEAU 2  = (1 2 1)

MATSEN OPERATOR ...

K =

 + (1 2) - (2 3) - (1 2 3) + (1 3 2)



CHI OPERATORS ...


CHI(1,1) =

 + 2*E + 2*(1 2) - (1 3) - (2 3) - (1 2 3)
 - (1 3 2)

CHI(1,2) =

 + E + (1 2) + (1 3) - 2*(2 3) + (1 2 3)
 - 2*(1 3 2)

CHI(2,1) =

 + E + (1 2) + (1 3) - 2*(2 3) - 2*(1 2 3)
 + (1 3 2)

CHI(2,2) =

 + 2*E - (1 2) + 2*(1 3) - (2 3) - (1 2 3)
```