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Configuration Interaction by the Method of Bonded Functions

Construction of a *Complete* and *Unique* List of Bonded Functions

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An approach is described to construct a complete and unique list of bonded functions for arbitrary spin states from any number of reference functions, any degree of orbital substitution, and any orbital pool.

Key words: Configuration interaction – Bonded functions

In a previous paper [1] a configuration interaction program has been described, and calculations have been presented, using the bonded functions formalism (the references to the earlier approaches to this problem can be found therein).

The bonded functions Φ have been introduced by Boys *et al.* [2] and are defined as follows

$$\Phi = \mathscr{A}[\phi_1\phi_2][\phi_3\phi_4] \ldots [\phi_{2p-1}\phi_{2p}][\phi_{2p+1} \ldots [\phi_n$$

where the spin coupled pairs are

$$\begin{aligned}[\phi_i\phi_j] &= \phi_i(i)\phi_j(j)(\alpha(i)\beta(j)-\beta(i)\alpha(j)) \qquad \phi_i \neq \phi_j \\ &= \phi_i(i)\phi_j(j)\alpha(i)\beta(j) \qquad \phi_i = \phi_j\end{aligned}$$

and the unpaired orbital is

$$[\phi_i = \phi_i(i)\alpha(i)$$

The symbol $\mathscr{A}$ denotes an antisymmetrizing operator that produces a normalized, completely antisymmetric wavefunction. The functions ϕ_i are assumed to be orthonormal. If $\phi_i = \phi_j$, then the orbitals must appear in the same spin coupled pair or the function vanishes.

A given set of orbitals ϕ may be bracketed together in a number of different ways. A linearly independent set of bonded functions (canonical set) may be formed according to the following rules: (a) In each bonded function identical orbitals must be bracketed together (spin coupled). (b) To the remaining orbitals the remaining left and right brackets must be assigned. These have to be assigned one to each orbital in all possible ways consistent with there being at least one more left bracket to the left of any right bracket than there are right brackets. The brackets are associated by the ordinary laws of algebra and the orbitals assigned to each pair of brackets, spin coupled. The excess of left brackets (if any) represents the uncoupled orbitals.

In actual applications one is usually faced with the problem to construct a *complete* and *unique* list of bonded functions of arbitrary spin state from a list of reference functions and a list of pool orbitals by substituting specified numbers of orbitals in the reference functions by pool orbitals. In the literature, so far, the list of bonded functions has always been assumed either to be given, or its construction to be trivial. Unfortunately, only approaches of constructing lists of bonded functions under various restrictions have been proposed and partly implemented [3]. The present note is just intended to demonstrate that the construction of a complete and unique list of bonded functions *without any restrictions* is trivial indeed.

The unique and complete list of bonded functions is generated by the following algorithm: For convenience, some *technical terms* are introduced first: The list of orbitals occupied in the bonded function (or in general in an electronic configuration), ordered according to increasing orbital sequence numbers q_i, doubly occupied orbitals listed twice, will be called an ordered orbital configuration Q, $Q=(q_0, q_1, \ldots, q_{n-1})$, $q_0 \leqslant q_1 \leqslant \ldots \leqslant q_{n-1}$. With each orbital configuration a characteristic number N may be associated $N=(q^{n-1}) \cdot q_{n-1} + \ldots + (q^1) \cdot q_1 + (q^0) \cdot q_0$, where the base q is one greater than the largest orbital sequence number in the complete orbital list. Alternatively, the orbital configuration may be specified in the occupation number representation. In this form, the list position denotes the orbital sequence number and the position value denotes the occupation number (0, 1, 2) of the orbital. Finally, the number of orbitals substituted in the reference function by pool orbitals will be called the *degree of substitution*.

One reference function is treated at a time. From the reference function an ordered orbital configuration is generated in the occupation number representation. From the orbital pool an orbital subpool is constructed in the occupation number representation, such that the sum of occupation numbers of each orbital in the reference function and in the orbital subpool is less than or equal two. This *guarantees* that for any generated configuration the occupation number of any orbital is less than or equal two. One degree of orbital substitution is treated at a time. Orbital configurations are generated by substituting the specified number of orbitals in the reference function by orbitals from the subpool for all combinations of reference orbitals, and all combinations of pool orbitals. This *guarantees* that the list of orbital configuration is complete. The sets of substituted orbitals and of substituting orbitals must have no common elements. This *guarantees* that the sets of orbital configurations generated from the same reference function by different degrees of orbital substitutions contain no common elements. The substitution is performed for each orbital substitution starting with the highest reference function orbital (sequence number) and with the lowest subpool orbital. This *guarantees* that the orbital configurations generated from each degree of orbital substitutions are ordered according to increasing characteristic numbers.

One orbital configuration is generated at a time. Orbital configurations with more identical orbital pairs than paired electrons are discarded. The orbital configuration symmetry class is conveniently determined at this place, if specified, and orbital configurations of symmetry classes not to be included are dropped. The lists of orbital configurations generated previously from reference functions different from the present, if any, are checked for identical orbital configurations (see below). For each *list* of orbital configurations generated from one reference state by one degree of orbital substitution each list of orbital configurations generated from each previous reference function and each degree of orbital substitution has to be searched *sequentially once*. This is true because the orbital configurations generated from each reference function by a given degree of orbital substitutions are ordered by increasing characteristic numbers. Orbital configurations identical to previously generated orbital configurations are discarded. This *guarantees* that the list of orbital configurations is unique. A list of orbital configurations is built and saved on external direct access storage for each reference function and each degree of orbital substitution.

For each (valid and unique) orbital configuration the complete canonical set of bonded functions is generated. A pattern of all canonical sets to be expected for the set of generated orbital configurations is constructed initially (by the method of bracket permutation) and is used subsequently to generate the complete canonical set of bonded functions from each orbital configuration.

The described procedure is performed for each reference function, and for each degree of orbital substitutions. The generated list of bonded functions is unique and complete.

This method has been implemented in the form described on an IBM 360/91 computer as part of the MUNICH quantum chemical program system [4]. The program has been written in IBM 360 Fortran, except for the direct access I/0 routine which is written in IBM 360 Assembler language in order to use direct track addressing. This routine can be substituted by a routine using the Fortran direct write/read facilities. The program has been fully tested for various spin states, reference functions, and number of orbital substitutions.

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