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Reduced-Density-Matrix Theory: The Electron-Pair Approximation

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The form of the K-space representation, Γ, of the 2-matrix for electronic wave functions, which depends strongly on the form of the wave function, is discussed. For Hartree-Fock functions Γ is diagonal, for antisymmetrized products of strongly orthogonal geminal (APSG) functions Γ has $N/2$ idempotent blocks plus diagonal terms, and for configuration interactions functions Γ is generally non-diagonal. A new proof of the special properties of Γ for APSG functions is given. The 2-matrix of the truncated natural orbital expansion of the Boys ^1S Be function is presented and discussed in view of the electron-pair approximation. The natural 3-state functions needed in the "1-3" natural expansion of Be are also presented.

On discute la forme de la représentation dans l'espace $K:\Gamma$, de la matricedensité du second ordre pour des fonctions d'onde électroniques; elle dépend fortement de la forme de la fonction d'onde. Pour des fonctions de Hartree-Fock Γ est diagonal, pour des produits antisymétrisés de fonctions géminales fortement orthogonales (APSG) Γ a $N/2$ blocs idempotents et des termes diagonaux, pour des fonctions d'interaction de configuration Γ est généralement non-diagonal. Une nouvelle preuve des propriétés spéciales de Γ pour les fonctions APSG est donnée. La matrice du second-ordre du développement tronqué de Boys en orbitales naturelles pour ^1S Be est présentée et discutée du point de vue de l'approximation par paires. Les fonctions naturelles a 3 états nécessaires au développement naturel „1-3" de Be sont aussi données.

Die Form der K-Raum-Darstellung, Γ, der Zweiermatrix für Elektronenwellenfunktionen, die stark von der Form der Wellenfunktion abhängt, wird diskutiert. Für Hartree-Fock-Funktionen ist Γ diagonal, für antisymmetriesierte Produkte von streng orthogonalen Geminalen (APSG) besteht Γ aus $N/2$ idempotenten Blöcken plus Diagonaltermen, und für Konfigurationswechselwirkungsfunktionen ist Γ allgemein nicht-diagonal. Für die speziellen Eigenschaften von Γ für APSG's wird ein neuer Beweis gegeben. Die Zweiermatrix der abgebrochenen Entwicklung natürlicher Orbitale der Boys'schen ^1S-Be-Funktionen wird angegeben und im Hinblick auf die Elektronenpaarapproximation diskutiert. Die in der natürlichen 1-3-Entwicklung von Be benötigten 3-Elektronen-Funktionen werden gleichfalls angegeben.

Introduction

Research on the theory of reduced-density-matrices is motivated primarily by the desirability of having a possible alternative to solving the Schrödinger equation in order to find mathematical descriptions of physical states of electronic systems (e.g., atoms or molecules). As is well known, it is impossible to solve the Schrödinger equation exactly for an N-electron system with $N > 1$. In principle, however, the approximation called the configuration interaction method can yield solutions which give expectation values of physical properties, generally the total energy, as accurately as experimental measurements. To date this accuracy has been achieved only for 2-electron systems, although with the advent of even larger and faster electronic computers such accuracy will probably be obtained for 3- and 4-electron systems in the near future. The problem of constructing a reduced-density-matrix for a state of interest, i.e., defining the necessary and sufficient conditions one must impose on a density matrix to insure a one-to-one correspondence with a quantum mechanical state, has been labeled "the N-representability problem" by COLEMAN [*5*]. The physical properties normally of interest are eigenvalues of one- and two-electron operators; therefore, one is concerned primarily with reduced-density-matrices of first- and second-order only.

The 2-Matrix

The second-order reduced-density-matrix, called the 2-matrix, is defined by

$$\Gamma(1,2;1',2') = \binom{N}{2} \int \Psi(1,2,3\ldots N)\,\Psi^*(1',2',3\ldots N)\,d\tau_3\ldots d\tau_N \tag{1}$$

where $\Psi(1,2,\ldots N)$ is an N-electron wave function and $\binom{N}{2}$ equals the number of ordered electron-pairs in the N-electron system (Löwdin's normalization) [*12*]. From its definition, $\Gamma(1,2;1',2')$ is a Hermitian quadratic kernel; thus it has a diagonal series representation [*8*],

$$\Gamma(1,2;1',2') = \sum_i \lambda_i\, g_i(1,2)\, g_i^*(1',2')\,, \tag{2}$$

where the set of functions g_i are normalized and antisymmetric with respect to interchange of variables; $g(1,2) = -g(2,1)$. Corresponding to the 2-matrix function, we can introduce the 2-matrix operator $\boldsymbol{\Gamma}^{(2)}$,

$$\boldsymbol{\Gamma}^{(2)} f(1,2) = \int \Gamma(1,2;1',2')\, f^*(1',2')\, d\tau_{1'}\, d\tau_{2'}\,, \tag{3}$$

where f is an arbitrary 2-variable function. The eigenvalue equation for the 2-matrix operator is

$$\boldsymbol{\Gamma}^{(2)} g_i(1,2) = \lambda_i\, g_i(1,2)\,. \tag{4}$$

The λ_i are eigenvalues and the g_i the corresponding eigenfunctions of $\boldsymbol{\Gamma}^{(2)}$. The g_i are called natural geminals; "geminal" referring to 2-electron function and "natural" referring to an eigenfunction of the reduced-density-operator. The eigenvalues λ_i may be interpreted as the number of electron-pairs described by g_i; the probability of an electron-pair being "in" g_i times the total density of electron-pairs in the N-electron system. (By the term "electron-pair" we shall always mean ordered pairs; i.e., the electrons "labeled" 1 and 2 form one pair.)

By introduction of the 2-matrix we transform the problem of studying N-electron functions into one of studying the properties of a set of invariant 2-electron functions — the natural geminals [*5*]. Once the natural geminals are known, any 2-electron properties can be obtained immediately. E.g., consider the N-electron Hamiltonian

$$H = \sum_{i=1}^{N} h_i^{(1)} + \sum_{i<j}^{N} h_{ij}^{(2)}\,, \tag{5}$$

which can be rewritten as [we divide by the norm of Γ (1,2)]

$$\mathscr{H} = \frac{1}{N-1}\left(h_1^{(1)} + h_2^{(1)}\right) + h_{12}^{(2)}\,. \tag{6}$$

The expectation value of $\mathscr{H}$ can be written as

$$\int \mathscr{H}\, \Gamma(1, 2; 1, 2)\, d\tau_1\, d\tau_2 = \sum_i^{r_2} \lambda_i\, \varepsilon_i\,, \tag{7}$$

where

$$\varepsilon_i = \int g_i^*(1, 2)\, \mathscr{H}\, g_i(1, 2)\, d\tau_1\, d\tau_2\,, \tag{8}$$

and r_2 is the 2-rank of Ψ [*1*].

One-electron properties are calculated via the 1-matrix which is obtained from the 2-matrix by an integration,

$$\Gamma(1; 1') = \frac{2}{N-1} \int \Gamma(1, 2; 1', 2)\, d\tau_2\,. \tag{9}$$

There is a great deal yet to be learned about the 2-matrix. Approximate natural geminals, and their corresponding eigenvalues, have been obtained for a number of 4-electron atomic and molecular wave functions [*3*] of varying degrees of goodness (with respect to the ground state total energy). It was seen that the properties of the 2-matrix vary greatly in going from the simple form of the Hartree-Fock function to configuration interaction functions. The natural geminals changed from a simple product to an extended sum of products. Both g_1 and g_2 include the terms which had been introduced into the original functions to describe electron-electron correlation effects. In the next section we will consider the special properties of the 2-matrix for the Be ^1S ground state when the 4-electron wave function is approximated as an antisymmetrized product of strongly orthogonal geminals (APSG). Functions of this form are intermediate between the Hartree-Fock and configuration interaction forms in complexity [*14*]. The formalism used is that developed by BARNETT and SHULL [*3*] which is quite useful because it allows direct general application of most of the results obtained by LÖWDIN and SHULL in their compleat study of the 2-electron system [*13*].

The Electron-Pair Approximation

It was shown by LÖWDIN [*12*] that an N-electron function can be expanded as a linear combination of Slater determinants,

$$\Psi(1, 2, 3, 4) = \sum_k d_k\, \Psi_k(1, 2, 3, 4)\,, \tag{10}$$

where the set of d_k, variationally determined coefficients, are chosen to give the proper symmetry properties to Ψ — e.g., for an atom, Ψ is generally an eigenfunction of the operators L^2, L_z, S^2, S_z. In forming the 2-matrix we first expand each Ψ_k across its first two rows, then we have

$$\Psi(1, 2, 3, 4) = \frac{1}{\sqrt{6}} \sum_{i,j} C_{ij}\, f_i(1, 2)\, f_i^*(3, 4)\,. \tag{11}$$

In matrix notation

$$\Psi = \frac{1}{\sqrt{6}} \boldsymbol{f}(1, 2)\, \boldsymbol{C} \boldsymbol{f}^\dagger(3, 4)\,, \tag{12}$$

where $\boldsymbol{f}$ is a row vector of all the 2 × 2 Slater determinants, the f_i, which result from the Laplace expansion on each Ψ_k above. Now the 2-matrix function is given by

$$\Gamma(1, 2; 1', 2') = \boldsymbol{f}(1, 2)\, \boldsymbol{C}\, \boldsymbol{C}^{\dagger} \boldsymbol{f}^{\dagger}(1', 2')\,, \tag{13}$$

where we have assumed orthonormality of the set used to construct Ψ, thus

$$\boldsymbol{f}^{\dagger}(3, 4)\, \boldsymbol{f}(3, 4) = \mathbf{1}\,. \tag{14}$$

After diagonalizing the K-space representation of $\Gamma(1, 2; 1', 2')$, $\boldsymbol{C}\, \boldsymbol{C}^{\dagger}$, the 2-matrix becomes

$$\Gamma(1, 2; 1', 2') = \boldsymbol{g}(1, 2)\, \boldsymbol{\lambda}\, \boldsymbol{g}^{+}(1', 2') = \sum_{i}^{r_2} \lambda_i\, g_i(1, 2)\, g_i^{*}(1', 2')\,. \tag{15}$$

(The reader will find the above procedure presented in considerable detail in Ref. [*3*].)

Now we consider the special case when Ψ is constructed via the APSG approximation [*14*]. The two pair-functions are defined by

$$\Lambda_A = \sum_{i=1}^{p} a_i [\varphi_{i_1}(1)\, \varphi_{i_2}(2)]\,, \tag{16}$$

and

$$\Lambda_B = \sum_{j=1}^{q} b_j [\theta_{j_1}(1)\, \theta_{j_2}(2)]\,, \tag{17}$$

where both functions are normalized and antisymmetric to electron exchange (the square bracket denotes a Slater determinant). The strong orthogonality condition which is always used in practice [*14*], i.e.

$$\int \Lambda_A(1, 3)\, \Lambda_B(3, 4)\, d\tau_3 = 0\,, \tag{18}$$

is introduced by assuming orthonormality within and between the 1-electron spinorbital sets $\{\varphi_i\}$ and $\{\theta_j\}$. Therefore,

$$\sum_{i}^{p} a_i^2 = 1\,, \tag{19}$$

$$\sum_{j}^{q} b_j^2 = 1\,, \tag{20}$$

and the 4-electron function is given by

$$\Psi(1, 2, 3, 4) = [\Lambda_A(1, 2)\, \Lambda_B(3, 4)]\,. \tag{21}$$

Expanding Ψ, Eq. (21), it has the form [*3*]

$$\begin{aligned} \Psi = \frac{1}{\sqrt{6}} \sum_{i,j} a_i\, b_j\, \{ & [\varphi_{i_1} \varphi_{i_2}]\, [\theta_{j_1}\, \theta_{j_2}] + [\theta_{j_1}\, \theta_{j_2}]\, [\varphi_{i_1} \varphi_{i_2}] + \\ & + [\varphi_{i_1}\, \theta_{j_2}]\, [\varphi_{i_2}\, \theta_{j_1}] + [\varphi_{i_2}\, \theta_{j_1}]\, [\varphi_{i_1}\, \theta_{j_2}] - \\ & - [\varphi_{i_1}\, \theta_{j_1}]\, [\varphi_{i_2}\, \theta_{j_2}] - [\varphi_{i_2}\, \theta_{j_2}]\, [\varphi_{i_1}\, \theta_{j_1}] \}\,, \end{aligned} \tag{22}$$

where the double sum is over the p terms in Λ_A, the q terms in Λ_B, and the $p \times q$ terms that are mixed (contain one spinorbital from each pair-function). Now, considering the matrix notation of Eq. (12), the row vector $\boldsymbol{f}(1, 2)$ can be grouped into terms from Λ_A, terms from Λ_B, and the mixed terms,

$$\boldsymbol{f} = \boldsymbol{f}^{A} \oplus \boldsymbol{f}^{B} \oplus \boldsymbol{f}^{M}\,. \tag{23}$$

Further, $\boldsymbol{C}$ has the form

$$\boldsymbol{C} = \begin{pmatrix} \boldsymbol{O} & \boldsymbol{C}^{AB} & \boldsymbol{O} \\ \boldsymbol{C}^{BA} & \boldsymbol{O} & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{C}^{MM} \end{pmatrix} . \tag{24}$$

Changing notation slightly, let

$$\boldsymbol{\Gamma}^{AB} = \boldsymbol{C}^{AB} (\boldsymbol{C}^{AB})^{\dagger} \tag{25}$$

with matrix elements

$$\Gamma_{ij}^{AB} = \sum_k C_{ik}^{AB} C_{jk}^{AB} . \tag{26}$$

Now the K-space representation of the 2-matrix has block diagonal form,

$$\boldsymbol{C}\boldsymbol{C}^{\dagger} = \boldsymbol{\Gamma} = \begin{pmatrix} \boldsymbol{\Gamma}^{AB} & \boldsymbol{O} & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{\Gamma}^{BA} & \boldsymbol{O} \\ \boldsymbol{O} & \boldsymbol{O} & \boldsymbol{\Gamma}^{MM} \end{pmatrix} . \tag{27}$$

Generally, to find the natural geminals we would need to diagonalize each block in turn. However, due to the special form of the APSG function we see that this is not necessary. Observing the following relationship,

$$\begin{aligned} (\Gamma^{AB})^2_{ij} &= \sum_n \Gamma_{in}^{AB} \Gamma_{nj}^{AB} \\ &= \sum_n \{\sum_k C_{ik}^{AB} C_{nk}^{AB}\} \{\sum_l C_{nl}^{AB} C_{jl}^{AB}\} \\ &= \sum_n \{\sum_k a_i b_k a_n b_k\} \{\sum_l a_n b_l a_j b_l\} \\ &= \sum_n a_i a_n^2 a_j \\ &= \Gamma_{ij}^{AB} , \end{aligned} \tag{28}$$

which is valid for all i and j, $\boldsymbol{\Gamma}^{AB}$ is an idempotent matrix,

$$(\boldsymbol{\Gamma}^{AB})^2 = \boldsymbol{\Gamma}^{AB} . \tag{29}$$

Therefore $\boldsymbol{\Gamma}^{AB}$ can have eigenvalues of zero and unity only [*8*]. From the trace of $\boldsymbol{\Gamma}^{AB}$,

$$\operatorname{Tr} \boldsymbol{\Gamma}^{AB} = \sum_i \Gamma_{ii}^{AB} = 1 , \tag{30}$$

it follows that $\boldsymbol{\Gamma}^{AB}$ has only one non-zero eigenvalue, $\lambda = 1$.

Considering the secular equation briefly [*8*], the set of numbers $\{a_i\}$ of Eq. (16) form the eigenvector and the eigenfunction may be chosen as Λ_A itself. The same procedure follows through for $\boldsymbol{\Gamma}^{BA}$ showing Λ_B to be its natural geminal.

Inspection of matrix elements for terms in $\boldsymbol{\Gamma}^{MM}$ shows that only diagonal terms appear because of the relationships among $\{\varphi_i\}$ and $\{\theta_j\}$. Further, from Eq. (22) the diagonal terms are degenerate in sets of four. The corresponding eigenfunctions are just the simple products, $[\varphi_i \theta_j]$, which KUTZELNIGG [*11*] calls "uncorrelated" natural geminals.

One can, by this method, go into considerably more detail than we have done here. By explicitly specifying the forms of Λ_A and Λ_B one can determine the 2-rank of Ψ [*1*] and enumerate the number and magnitudes of all the eigenvalues of $\boldsymbol{\Gamma}$. One can continue, generalizing the results to N-electron systems, consider states of different symmetries, and consider systems of chemically different types. The theorem proved above, that the 2-matrix of a APSG wave function is diagonal, it not new, although the method of proof is. KUTZELNIGG [*10*, *11*] has considered the problem and spelled out many of the special relationships implicit in the theorem. (The reader is referred to Ref. [*11*] where he reviews, lists, and discusses many of these properties.)

Natural Geminals

Considerable insight can be gained by studying a wave function expressed in an invariant basis set. In this section, then, we present the results of a 2-matrix analysis of the Boys ^1S ground state configuration interaction wave function [*4*] expressed in its natural orbital expansion [*2*]. Clearly, this natural orbital set is only approximate, however, the utility of transforming functions to such a basis is well established [*9*, *15*]. The natural orbital expansion is given in Tab. 1, and the eigenvalues of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ are listed in Tab. 2.

The natural geminals (see Tab. 3) are seen to have forms close to what one would expect from an APSG function. For an APSG function the natural orbitals of Λ_A and Λ_B are the natural orbitals of Ψ as well [*11*]. We see here that, except for small cross-terms containing χ_4, g_1 and g_2 are sums of squares — the natural expansion form for 2-electron functions. From its use in the natural orbital expansion, χ_4 is what one would call an intershell orbital. If Ψ were a pure APSG form, all natural orbitals would be localized within the region spanned by Λ_A or Λ_B only, and intershell correlation effects would be described only by uncorrelated natural geminals such as the dominant term in g_3. If one compares the natural orbitals of the EBBING and HENDERSON [7] APSG calculation of LiH with the natural orbitals expressed in the same basis of Ebbing's configuration interaction calculation [*6*] of the same molecule, the strongly occupied inner shell (essentially a Li^{++} 1s orbital) and bonding natural orbitals (see Ebbing's plot of σ_2) are quite similar. The delocalized natural orbitals of the configuration interaction function are transformed among themselves in the APSG function into orbitals within the space of Λ_A or Λ_B.

Table 1. *The truncated natural orbital expansion of the Boys* Be ^1S *function*[a]

	Configuration		Coefficient
1	$(\chi_1)^2\,(\chi_2)^2$	s^2s^2	0.954452
2	$(\chi_1)^2\,(\chi_3)^2$	s^2p^2	−0.296472
3	$(\chi_2)^2\,(\chi_4)^2$	s^2s^2	−0.023838
4	$(\chi_2)^2\,(\chi_5)^2$	s^2p^2	−0.023518
5	$(\chi_5)^2\,(\chi_2\chi_4)$	p^2s^2	−0.001157
6	$(\chi_1)^2\,(\chi_4)^2$	s^2s^2	−0.001157
7	$(\chi_3)^2\,(\chi_1\chi_4)$	p^2s^2	0.000895
8	$(\chi_2)^2\,(\chi_1\chi_4)$	s^2s^2	−0.000285
9	$(\chi_4)^2\,(\chi_1\chi_2)$	s^2s^2	−0.000114
10	$(\chi_1)^2\,(\chi_4\chi_6)$	s^2s^2	−0.000050

[a] See Ref. [*4*].

Table 2. *Occupation numbers for the Boys* ^1S Be *function*

$\Gamma^{(1)}$		$\Gamma^{(2)}$		
n	symmetry	λ		symmetry
.998877	s	.9999518		^1S
.912102	s	.9998465		^1S
.087896	p	$.9109798_3$		^1S
.000571	s	$.9109798_0$	(3)[b]	^3S
.000554	p	.0878962	(4)[c]	P
.000000	s			

[a] These values are for the total Ψ, for the truncated natural orbital expansion of Tab. 1 the numbers are the same through the sixth decimal.

[b] A 3-fold degenerate term (see Ref. [*3*]).

[c] A 4-fold term.

To the degree of degeneracy of the eigenvalues of g_1 and g_2, the sum and the difference of the first two natural geminals transform into predominantly K shell and L shell pair functions,

$$\frac{1}{\sqrt{2}}(g_1 + g_2) \sim \Lambda_K = 1.0\chi_1^2 - .02\chi_4^2 + .02\chi_5^2 - .0006\chi_1\chi_4$$

$$\frac{1}{\sqrt{2}}(g_1 - g_2) \sim \Lambda_L = .9\chi_2^2 - .3\chi_3^2 - .0004\chi_2\chi_4\,. \tag{31}$$

Omitting the cross-terms, an ASPG function formed from Λ_K and Λ_L gives the first four terms of the natural orbital expansion which has an overlap of almost unity with the total function [*2*]. (Of course starting from Λ_K and Λ_L as defined here, the overlap would be different as the coefficients in the natural orbital expansion are determined by a different criterion.) Similarly, the first few terms, the predominant ones, of the natural orbital expansions of WATSON's [*16*] and WEISS' [*17*] functions would be obtained by constructing Λ_K from χ_1, χ_4, χ_5 for WATSON, and from χ_1, χ_5, χ_6 for WEISS, and constructing Λ_L from χ_2, χ_3, χ_6 for WATSON and from χ_2, χ_3, χ_4 for WEISS. (In each case, χ_i refers to the i^{th} approximate natural orbital of the particular approximate function for Be [*2*].)

So we see that the form of the strongly occupied natural geminals for ^1S Be varies considerably, depending upon the model used to construct the wave function. For independent electrons we have $g_1 \sim [1s^2]$, $g_2 \sim [2s^2]$, or any linear combination of the two due to the eigenvalue degeneracy. For independent electron-pairs, $g_1 \sim \Lambda_K$, $g_2 \sim \Lambda_L$ — or again any linear combination. Then, in the more general configuration interaction function when intershell terms are introduced, mixing of the pairs will necessarily arise, and

$$g_1 \sim \frac{1}{\sqrt{2}}(\Lambda_K + \Lambda_L)$$

$$g_2 \sim \frac{1}{\sqrt{2}}(\Lambda_K - \Lambda_L)\,. \tag{32}$$

For the first two cases, the third natural geminal is similar, an uncorrelated product $[1s\,2s]$, while for configuration interaction functions it is considerably more complicated.

Table 3. *The natural geminals of the Boys truncated natural orbital expansion*[a]

Eigenvalues	.9999518 $g_1(^1S)$	.9998465 $g_2(^1S)$	$.9109798_3$ $g_3(^1S)$	$.9109798_0$ $g_4(^3S)$
$(\chi_1\chi_{\bar{1}})$	.70674	.70675	.00006	
$(\chi_1\chi_{\bar{2}})$	−.00000	−.00000	.99971	.99999
$(\chi_2\chi_{\bar{2}})$	.67534	−.67535	−.00001	
$(\chi_3\chi_{\bar{3}})$	−.20953	.20955	.00001	
$(\chi_2\chi_{\bar{4}})$	.00004	−.00004	−.00021	−.00020
$(\chi_4\chi_{\bar{4}})$	−.01692	−.01528	.00012	
$(\chi_5\chi_{\bar{5}})$	−.01588	−.01588	.00000	
$(\chi_1\chi_{\bar{4}})$	−.00038	−.00038	.00002	.00002
$(\chi_1\chi_{\bar{6}})$	−.00000	.00000	−.00000	−.00000
$(\chi_4\chi_{\bar{6}})$	−.00003	.00004	.00000	.00000
$(\chi_2\chi_{\bar{6}})$	−.00000	.00000	.00000	

Eigenvalues	$.9109798_0$	.0878962			
	$g_5(^3S)$, $g_6(^3S)$	$g_7(^1P)$, $g_8(^3P)$		$g_9(^3P)$, $g_{10}(^3P)$	
$(\chi_1\chi_2)$[b]	.99999	$(\chi_1\chi_3)$	.99999	$(\chi_1\chi_3)$[b]	.99999
$(\chi_2\chi_4)$	.00021	$(\chi_3\chi_4)$	−.00213	$(\chi_3\chi_4)$	.00213
$(\chi_1\chi_4)$	.00002	$(\chi_2\chi_3)$	−.00002	$(\chi_2\chi_3)$	−.00002
$(\chi_1\chi_6)$	−.00000				
$(\chi_4\chi_6)$	.00000				

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[a] $(k\bar{k})$ is a 2×2 Slater determinant. The term $(k\bar{l}) = (2)^{-1/2}[(k\bar{l}) \pm (l\bar{k})]$ with the $(+)$ for the singlet and $(-)$ for triplet symmetry. The bar denotes β spin; $(k\bar{k}) = (k\alpha\ k\beta)$.

[b] There is one vector for $\alpha\alpha$ spin and another for $\beta\beta$ spin.

Table 4. *The natural 3-state functions*[a]

	G_1	G_2		G_3	
Eigenvalues	0.998877	0.912102		0.087896	
Configurations	Coefficients	Configurations	Coefficients	Configurations	Coefficients
$(\chi_{\bar{1}}\chi_2\chi_{\bar{2}})$	.95499	$(\chi_{\bar{2}}\chi_1\chi_{\bar{1}})$	.99938	$(\chi_{\bar{3}}\chi_1\chi_{\bar{1}})$	−.99999
$(\chi_{\bar{1}}\chi_3\chi_{\bar{3}})$	−.29664	$(\chi_{\bar{2}}\chi_4\chi_{\bar{4}})$	−.02496	$(\chi_{\bar{3}}\chi_4\chi_{\bar{4}})$	.00302
$(\chi_{\bar{1}}\chi_4\chi_{\bar{4}})$	−.00116	$(\chi_{\bar{2}}\chi_5\chi_{\bar{5}})$	−.02462	$(\chi_{\bar{3}}\chi_1\chi_{\bar{2}})$	.00003
$(\chi_{\bar{4}}\chi_3\chi_{\bar{3}})$	.00063	$(\chi_{\bar{4}}\chi_5\chi_{\bar{5}})$	−.00086	$(\chi_{\bar{3}}\chi_1\chi_{\bar{4}})$	−.00000
$(\chi_{\bar{4}}\chi_2\chi_{\bar{2}})$	−.00020	$(\chi_{\bar{1}}\chi_4\chi_{\bar{4}})$	−.00008		
$(\chi_{\bar{2}}\chi_4\chi_{\bar{4}})$	−.00008	$(\chi_{\bar{6}}\chi_4\chi_{\bar{4}})$	−.00003		
$(\chi_{\bar{2}}\chi_3\chi_{\bar{3}})$	.00001	$(\chi_{\bar{6}}\chi_5\chi_{\bar{5}})$	−.00003		
$(\chi_{\bar{2}}\chi_5\chi_{\bar{5}})$	−.00000	$(\chi_{\bar{4}}\chi_1\chi_{\bar{1}})$	.00002		
$(\chi_{\bar{1}}\chi_4\chi_{\bar{6}})$	−.00005	$(\chi_{\bar{1}}\chi_3\chi_{\bar{3}})$	.00001		
$(\chi_{\bar{1}}\chi_2\chi_{\bar{4}})$	.00003	$(\chi_{\bar{1}}\chi_5\chi_{\bar{5}})$	−.00000		
$(\chi_{\bar{4}}\chi_2\chi_{\bar{6}})$	.00000	$(\chi_{\bar{6}}\chi_1\chi_{\bar{1}})$	−.00000		
$(\chi_{\bar{1}}\chi_2\chi_{\bar{6}})$	−.00000	$(\chi_{\bar{2}}\chi_1\chi_{\bar{4}})$	−.00030		
		$(\chi_{\bar{6}}\chi_1\chi_{\bar{4}})$	.00000		
		$(\chi_{\bar{2}}\chi_4\chi_{\bar{6}})$	.00000		

Table 4 (Continued)

Eigenvalues	G_4 0.000571	G_5 0.000554		G_6 0.000000	
Configurations	Coefficients	Configurations	Coefficients	Configurations	Coefficients
$(\chi_{\bar{4}}\chi_2\chi_{\bar{2}})$	−.99784	$(\chi_{\bar{5}}\chi_2\chi_{\bar{2}})$	−.99882	$(\chi_{\bar{4}}\chi_1\chi_{\bar{1}})$	−.70272
$(\chi_{\bar{2}}\chi_5\chi_{\bar{5}})$	−.03424	$(\chi_{\bar{5}}\chi_4\chi_{\bar{4}})$	−.04914	$(\chi_{\bar{2}}\chi_4\chi_{\bar{4}})$	−.50564
$(\chi_{\bar{4}}\chi_1\chi_{\bar{1}})$	−.04843	$(\chi_{\bar{5}}\chi_2\chi_{\bar{4}})$	−.00149	$(\chi_{\bar{2}}\chi_5\chi_{\bar{5}})$	−.49170
$(\chi_{\bar{1}}\chi_3\chi_{\bar{3}})$	.02650	$(\chi_{\bar{5}}\chi_2\chi_{\bar{6}})$	−.00119	$(\chi_{\bar{4}}\chi_2\chi_{\bar{2}})$	.06967
$(\chi_{\bar{1}}\chi_2\chi_{\bar{2}})$	−.00841	$(\chi_{\bar{5}}\chi_1\chi_{\bar{2}})$	−.00013	$(\chi_{\bar{2}}\chi_1\chi_{\bar{1}})$	.05574
$(\chi_{\bar{6}}\chi_1\chi_{\bar{1}})$	−.00146			$(\chi_{\bar{2}}\chi_1\chi_{\bar{4}})$	−.02787
$(\chi_{\bar{2}}\chi_1\chi_{\bar{1}})$	.00084				
$(\chi_{\bar{4}}\chi_5\chi_{\bar{5}})$	−.00117				
$(\chi_{\bar{6}}\chi_2\chi_{\bar{2}})$	.00013				
$(\chi_{\bar{4}}\chi_3\chi_{\bar{3}})$	−.00004				
$(\chi_{\bar{4}}\chi_1\chi_{\bar{2}})$	−.00477				
$(\chi_{\bar{4}}\chi_2\chi_{\bar{6}})$	−.00151				
$(\chi_{\bar{1}}\chi_2\chi_{\bar{6}})$	.00013				

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[a] Configurations $(\bar{a}c\bar{c})$ are 3 × 3 Slater determinants, while $(\bar{a}b\bar{c}) = (2)^{-1/2}((\bar{a}bc) - (a\overline{bc}))$.

Natural Expansions

Returning to the natural orbital expansion briefly, it should be noted that while it is the most rapidly convergent configuration interaction function, as proved by Löwdin [*12*], it is generally not as simple in form as the natural expansion of a function (for 2-electron functions the two are identical). The natural expansion is defined as the best least-squares expansion of Ψ in terms of eigenfunctions of $\Gamma^{(p)}$ and $\Gamma^{(N-p)}$ [*13*]. For $N > 2$, the natural expansion involving natural orbitals also involves eigenfunctions of $\Gamma^{(N-1)}$. For example, here the "1-3" natural expansion, in terms of eigenfunctions of $\Gamma^{(1)}$ and $\Gamma^{(3)}$, will have the form

$$\Psi = \frac{1}{\sqrt{4}} \sum_i C_i \chi_i(1)\, G_i(2, 3, 4)\,, \tag{33}$$

where the G_i are natural 3-state functions. In Tab. 4 the G_i of Boys natural orbital expansion function are given. It is clear that going from the "1-3" natural expansion, expanding and collecting terms, to the natural orbital expansion eliminates the simplicity of functional form.

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