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# Spin-Free Self-Consistent-Field Theory

R. D. Poshusta
*Department of Chemistry and Department of Physics, Washington State University, Pullman, Washington*
AND
R. W. Kramling
*Department of Chemistry, Washington State University, Pullman, Washington*

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Hartree–Fock (HF) equations are derived for an $N$-electron system with a spin-free Hamiltonian. All eigenstates of $S^2$ are considered for both open- and closed-shell states. States which possess two or more spin-coupling schemes (structures) are treated by mixed-structure kets. A procedure to optimize the mixture of structures is incorporated into the HF equations. A certain mixed-structure ket called the immanant is defined and used to derive the HF equations for a spin-projected Slater determinant. The conventional equations for single determinants and doubly occupied orbitals are derived as special cases. The spin-free method is used throughout: Permutational symmetry of a spin-free ket establishes the corresponding spin eigenvalue.

## INTRODUCTION

In the conventional approach to self-consistent-field (SCF) theory,[1,2] one constructs a wave function from one or more Slater determinants. One then derives an expression for the nonrelativistic energy of a system in terms of the spin-free orbitals. In the process the spin is completely eliminated by integration. Since the spin plays no dynamical role (as seen from the energy expression) it seems desirable for the sake of purity to eliminate spin from the beginning. In this paper we carry out this program.

A stronger motivation for eliminating spin in SCF theory is the ease with which "pure spin" states can be handled in the spin-free framework. The role of eigenkets of $S^2$ is taken over in the spin-free method by spin-free kets with irreducible symmetry under the symmetric group $S_N$. Such a spin-free ket is equivalent to a spin eigenket for every spin-free observable. Matsen[3] and his collaborators have used the spin-free method to advantage in such diverse applications as atomic and molecular calculations,[4] generalized Pauling numbers,[5] density-matrix theory[6,7] and even formulating an explicit spin property: spin density.[8] In this paper we apply the spin-free method to the derivation of SCF equations.

Matsen and Cantu[9] have given a careful symmetry analysis of the various types of SCF theory. The present paper is devoted exclusively to spin-free SCF theory.

Our method parallels the derivations of Roothaan[1,2] and can be outlined as follows:

(1) Select a product of orthonormal spin-free orbitals (singly or doubly occupied). (2) Project from the orbital product its component(s) with pure permutational symmetry. *Since the permutational symmetry of a spin-free ket determines the spin eigenvalues of the corresponding spin ket, the projected spin-free ket will give the same energy as a pure spin eigenket.* (3) Find the energy expression $\langle H\rangle$ over the spin-free ket. (4) Conduct a variation of the orbitals to minimize the energy and thereby produce a set of spin-free Hartree–Fock equations for the optimum spin-free orbitals.

Our equations could have been derived from the conventional spin kets as has been done in certain special cases. We find the spin-free approach considerably simpler than the corresponding derivation from the spin route. Despite the equivalence of our approach and the spin approach we call our equations spin-free SCF equations.

## IMMANANT WAVE FUNCTIONS

Consider the product of $N$ distinct and orthonormal spin-free orbitals (double occupancy will be discussed in a later section):

$$|\Phi\rangle \equiv |\varphi_1\rangle|\varphi_2\rangle\cdots|\varphi_N\rangle. \tag{1}$$

Here $|\varphi_1\rangle$ represents the state of electron one, $|\varphi_2\rangle$ that of electron two, etc. If the Hamiltonian of the system commutes with all permutations of the electrons (the electrons are indistinguishable) then it follows that the eigenkets of the system have irreducible permutational symmetry. Hence, to approximate such an eigenket we must project $|\Phi\rangle$ onto its irreducible com-

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[1] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

[2] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

[3] F. A. Matsen, *Advances in Quantum Chemistry*, edited by Per O. Löwdin (Academic Press Inc., New York, 1964), Vol. I; also F. A. Matsen and R. D. Poshusta, Tech. Rep. of the Molecular Phys. Group, U. of Texas, Austin, Tex., 1965 (unpublished).

[4] For orbital products, the spin-free method possesses no computational advantages over the linear combination of Slater determinants. Recently, one of the authors (RDP) has used the method for many-electron calculations (unpublished) with Singer-type "polymals." K. Singer, Proc. Roy. Soc. (London) **A258**, 412 (1960). See also I. G. Kaplan, Tekhno. Theoret. Exp. Chem. **1**, 619 (1965).

[5] F. A. Matsen, A. A. Cantu, and R. D. Poshusta, J. Phys. Chem. **70**, 1558 (1966).

[6] R. D. Poshusta and F. A. Matsen, J. Math. Phys. **7**, 711 (1966).

[7] R. D. Poshusta, J. Math, Phys. **8**, 955 (1967).

[8] F. A. Matsen and A. A. Cantu, J. Phys. Chem. **72**, 21 (1968).

[9] F. A. Matsen and A. A. Cantu, J. Phys. Chem. (to be published).

ponents. The simplest projector[10] for this is the "principle idempotent" defined by

$$e^{\alpha}\equiv\frac{f^{\alpha}}{N!}\sum_{P}\chi_{P}{}^{\alpha}P, \tag{2}$$

where the sum is taken over all permutations, $P$, of $S_N$. The projection defined by[10]

$$|\Phi;\alpha\rangle\equiv\frac{\sqrt{N!}}{f^{\alpha}}e^{\alpha}|\Phi\rangle \tag{3}$$

is called the immanant[11] of $|\Phi\rangle$. When $\alpha=\{1^N\}$, the characters $\chi_P{}^{\alpha}$ become $\epsilon_P$ (the parity of $P$) and $|\Phi;\{1^N\}\rangle$ is a determinant. When $\alpha=\{N\}$ the characters $\chi_P{}^{\alpha}$ become 1, and $|\Phi;\{N\}\rangle$ is a permanant.

For electrons, the Pauli principle excludes all permutational symmetries except those of the form[3]

$$\alpha=\{2^p,1^{N-2p}\}, \tag{4}$$

where $p$ is variously called the permutation quantum number, the pair quantum number, or the number of bonds, and $N-2p$ is sometimes called the valence of the "permutation state" $|\Phi;\alpha\rangle$. The spin quantum number of the corresponding spin eigenket is given by

$$S=\tfrac{1}{2}N-p. \tag{5}$$

The immanant $|\Phi;\alpha\rangle$ plays the same role for spin-free SCF theory as the single-Slater determinant plays for the conventional SCF theory with this important difference: $|\Phi;\alpha\rangle$ *always* represents a pure spin state. Harris[12] has shown that the immanant projector, $e^{\alpha}$, is the spin-free counterpart of Löwdin's[13] projection operator, $O_s$.

Now let $H$ be any linear operator which commutes with all permutations, $HP=PH$. The expectation value of $H$ over the immanant of $|\Phi\rangle$ is given by

$$\begin{aligned}\langle H\rangle&=\langle\Phi;\alpha|H|\Phi;\alpha\rangle\\&=\frac{N!}{(f^{\alpha})^2}\langle\Phi|He^{\alpha}|\Phi\rangle\\&=\frac{1}{f^{\alpha}}\sum_{P}\chi_P{}^{\alpha}\langle\Phi|HP|\Phi\rangle.\end{aligned} \tag{6}$$

When $H$ is the identity operator we find that our immanant is normalized:

$$\begin{aligned}\langle 1\rangle&=\langle\Phi;\alpha|\Phi;\alpha\rangle\\&=\frac{1}{f^{\alpha}}\sum_{P}\chi_P{}^{\alpha}\langle\Phi|P|\Phi\rangle.\end{aligned}$$

Since the orbitals are distinct and orthonormal, only the identity permutation contributes a nonzero term to the sum. By definition $f^{\alpha}\equiv\chi_{g}{}^{\alpha}$ so that $\langle 1\rangle=1$.

The spin-free Hamiltonian of an $N$-electron system is assumed to have the form

$$H=\sum_{i=1}^{N}h_i+\tfrac{1}{2}\sum_{i\neq j}^{N}g_{ij}. \tag{7}$$

The energy expression for the immanant now becomes

$$E_{\alpha}=\frac{1}{f^{\alpha}}\sum_{P}\chi_P{}^{\alpha}\Big[\sum_{i}\langle\Phi|h_iP|\Phi\rangle+\tfrac{1}{2}\sum_{i\neq j}\langle\Phi|g_{ij}P|\Phi\rangle\Big].$$

Again the orthonormality of the orbitals simplifies this expression as in the conventional spin formulation to

$$E_{\alpha}=\sum_{i}H_i+\tfrac{1}{2}\sum_{i\neq j}\left(J_{ij}+\frac{\chi_2{}^{\alpha}}{f^{\alpha}}K_{ij}\right), \tag{8}$$

where

$$H_i\equiv\langle\varphi_i|h|\varphi_i\rangle,$$

$$J_{ij}\equiv\langle\varphi_i\varphi_j|g|\varphi_i\varphi_j\rangle,$$

and

$$K_{ij}\equiv\langle\varphi_i\varphi_j|g|\varphi_j\varphi_i\rangle.$$

The coefficient $\chi_2{}^{\alpha}/f^{\alpha}$ is the ratio of the character of transpositions to the character of the identity. This ratio measures the degree of permutation correlation[6] in the immanant. When $\alpha=\{1^N\}$, $\chi_2{}^{\alpha}/f^{\alpha}=-1$, the correlation is greatest and if $K_{ij}>0$ the energy is lowest. For other symmetries, $\alpha$, the correlation decreases (the energy increases) until the extreme case $\alpha=\{N\}$ is reached when $\chi_2{}^{\alpha}/f^{\alpha}=1$. This ordering of energies due to correlation is known as Hund's rule. It is often stated in the spin form: States of highest multiplicity lie lowest.

## SPIN-FREE SCF EQUATIONS FOR IMMANANTS

Spin-free self-consistent-field theory for immanants results when we ask for the orbitals which minimize the spin-free energy expression, Eq. (8). The minimization procedure is very familiar from the conventional SCF theory.[1] Let $|\delta\varphi_i\rangle$ be an arbitrary variation of the orbitals $|\varphi_i\rangle$. The energy expression then undergoes a variation $\delta E_{\alpha}$ given by

$$\begin{aligned}\delta E_{\alpha}=&\sum_{i}\langle\delta\varphi_i|h+\sum_{j\neq i}\left(J_j+\frac{\chi_2{}^{\alpha}}{f^{\alpha}}K_j\right)|\varphi_i\rangle\\&+\sum_{i}\langle\varphi_i|h+\sum_{j\neq i}\left(J_j+\frac{\chi_2{}^{\alpha}}{f^{\alpha}}K_j\right)|\delta\varphi_i\rangle,\end{aligned} \tag{9}$$

where for convenience we have defined the operators $J$ and $K$ by

$$\langle\varphi_k|J_j|\varphi_i\rangle\equiv\langle\varphi_k\varphi_j|g|\varphi_i\varphi_j\rangle \tag{10}$$

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[10] For a description of permutations, permutation algebras and the transformations of $N$-electron kets by permutations, see Ref. 3.

[11] D. E. Littlewood, *The Theory of Group Characters* (Clarendon Press, Oxford, England, 1940).

[12] F. Harris, *Advances in Quantum Chemistry*, edited by P. O. Löwdin (Academic Press Inc., New York, 1967), Vol. 3.

[13] P. O. Löwdin, Phys. Rev. **97**, 1509 (1955).

and

$$\langle\varphi_k|K_j|\varphi_i\rangle\equiv\langle\varphi_k\varphi_j|g|\varphi_j\varphi_i\rangle.$$

The variation must be conducted subject to the condition that the orbitals remain orthonormal:

$$\langle\delta\varphi_i|\varphi_j\rangle+\langle\varphi_i|\delta\varphi_j\rangle=0. \tag{11}$$

We introduce the matrix of Lagrangian multipliers, $\epsilon_{ij}$, and require that

$$\delta E_\alpha'=\delta E_\alpha-\sum_{ij}\epsilon_{ij}(\langle\delta\varphi_i|\varphi_j\rangle+\langle\varphi_i|\delta\varphi_j\rangle)$$

should vanish. Hence, in the usual way we find the spin-free Hartree-Fock equations

$$\left[h+\sum_{j\neq i}\left(J_j+\frac{\chi_2^\alpha}{f^\alpha}K_j\right)\right]|\varphi_i\rangle=\sum_j\epsilon_{ji}|\varphi_j\rangle. \tag{12}$$

The spin-free immanant Fock operator may be introduced:

$$F^\alpha|\varphi_i\rangle=\sum_j\epsilon_{ji}|\varphi_j\rangle, \tag{13}$$

where

$$F^\alpha\equiv L+\sum_j\left(J_j+\frac{\chi_2^\alpha}{f^\alpha}K_j\right).$$

and

$$L|\varphi_i\rangle\equiv h|\varphi_i\rangle-\left(1+\frac{\chi_2^\alpha}{f^\alpha}\right)\langle\varphi_i|g|\varphi_i\varphi_i\rangle.$$

Only in special cases is it possible to transform Eq. (13) into an eigenfunction-eigenvalue equation. For example, suppose $\alpha=\{1^N\}$ which means our immanant becomes a determinant (maximum multiplicity). Then $\chi_2^\alpha/f^\alpha=-1$ and $L=h$ so that Eq. (13) becomes

$$[h+\sum_j(J_j-K_j)]|\varphi_i\rangle=\sum_j\epsilon_{ji}|\varphi_j\rangle. \tag{14}$$

Now recall that the determinant is that immanant which is left unchanged (except for phase) by all unitary transformations of orbitals. In particular, we may apply that transformation which diagonalizes the $\epsilon_{ij}$'s. At the same time $\sum_j(J_j-K_j)$ is left invariant by a unitary transformation of orthonormal orbitals.[1] Hence in this case Eq. (13) becomes

$$F|\varphi_i\rangle=\epsilon_i|\varphi_i\rangle.$$

This is the familiar result from the conventional theory applied to a single-Slater determinant with all spins parallel.

## STRUCTURE KETS

In general $|\Phi\rangle$ has several independent components with permutational symmetry $\alpha$. These components correspond to the independent spin-coupling schemes for eigenkets of $S^2$. The immanant is an arbitrary (but simple) choice of one such component. The best spin-free ket is that particular component which gives the lowest energy. To find this component we introduce the spin-free structure kets.[3]

Within a given permutational symmetry $\alpha$, a structure projector, denoted by $\kappa$, is defined in terms of permutations. This operator has been thoroughly discussed in other places[3–5] and will not be defined here. A pure structure component of $|\Phi\rangle$ is defined to be

$$|\Phi;\kappa\rangle\equiv\kappa|\Phi\rangle. \tag{15}$$

There are $f^\alpha$ independent pure structure components of $|\Phi\rangle$ (or fewer if $|\Phi\rangle$ contains repeated orbitals) each of which corresponds to a different spin-coupling scheme in the conventional formulation. To find the closest approximation to the true Hamiltonian eigenket we must optimize the linear coefficients $\tau_\kappa$ in the mixed structure ket:

$$|\Phi;\boldsymbol{\tau}\rangle\equiv\sum_\kappa\tau_\kappa|\Phi;\kappa\rangle. \tag{16}$$

To find the norm of $|\Phi;\boldsymbol{\tau}\rangle$ we form

$$\langle\Phi;\boldsymbol{\tau}|\Phi;\boldsymbol{\tau}\rangle=\sum_\kappa\sum_{\kappa'}\tau_\kappa^*\tau_{\kappa'}\langle\Phi|\kappa^\dagger\kappa'|\Phi\rangle. \tag{17}$$

Since each of $\kappa^\dagger$ and $\kappa'$ are linear combinations of permutations, their product can be written in the form

$$\kappa^\dagger\kappa'=\sum_P(P)_{\kappa\kappa'}P, \tag{18}$$

where $(P)_{\kappa\kappa'}$ is a numerical coefficient called a Pauling number.[5] When Eq. (18) is substituted into Eq. (17) we find

$$\langle\Phi;\boldsymbol{\tau}|\Phi;\boldsymbol{\tau}\rangle=\sum_P T_P\langle\Phi|P|\Phi\rangle, \tag{19}$$

where[14]

$$T_P\equiv\sum_\kappa\sum_{\kappa'}\tau_\kappa^*(P)_{\kappa\kappa'}\tau_{\kappa'}. \tag{20}$$

Once again, the orthonormality of orbitals annihilates all terms of Eq. (19) except that contributed by the identity. Hence the norm becomes

$$\langle\Phi;\boldsymbol{\tau}|\Phi;\boldsymbol{\tau}\rangle=T_{\mathcal{I}}.$$

We adopt the normalizing condition

$$\begin{aligned}T_{\mathcal{I}}&=\sum_\kappa\sum_{\kappa'}\tau_\kappa^*(\mathcal{I})_{\kappa\kappa'}\tau_{\kappa'}\\&=1\end{aligned} \tag{21}$$

on the coefficients $\tau_\kappa$.

The expectation value of the Hamiltonian, Eq. (7), on the mixed structure ket is given by

$$E_\tau=\sum_i H_i+\tfrac{1}{2}\sum_{i\neq j}(J_{ij}+T_{(ij)}K_{ij}). \tag{22}$$

Equation (22) was derived in the same way as Eq. (8) was derived for the immanant. The degree of correla-

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[14] The coefficients $T_p$ are intimately related to the "Sanibel coefficients," denoted by $\langle\Theta|O_SP|\Theta\rangle$, and might be called spin-free Sanibel coefficients. See F. Sasaki and K. Ohno J. Math. Phys. 4, 1140 (1963).

tion in the mixed structure is determined by the coefficients $\tau_\kappa$. We will vary these coefficients [subject to the normalizing condition, Eq. (21)] to optimize the energy.

Let $\delta\boldsymbol{\tau}$ be an arbitrary variation in $\boldsymbol{\tau}$. Then the corresponding variation in $E_\tau$ is

$$\delta E_\tau = \tfrac{1}{2} \sum_{i\neq j} [\delta T_{(ij)}] K_{ij}.$$

The norm of $|\Phi;\boldsymbol{\tau}\rangle$ will be unchanged if $\delta T_{\mathcal{I}}=0$. Hence we introduce the Lagrangian multiplier $\theta$ and require that

$$\delta E' = \delta E_\tau - \theta \delta T_{\mathcal{I}}$$

should vanish. This leads to the equation

$$\tfrac{1}{2}\sum_{\kappa} \delta\tau_\kappa^* [\sum_{\kappa'} (\sum_{ij} K_{ij}(ij)_{\kappa\kappa'} - \theta(\mathcal{I})_{\kappa\kappa'})\tau_{\kappa'}] + \text{c.c.} = 0. \quad (23)$$

Since the variations $\delta\tau_\kappa^*$ are arbitrary we find

$$\sum_{\kappa'} (\sum_{ij} K_{ij}(ij)_{\kappa\kappa'} - \theta(\mathcal{I})_{\kappa\kappa'})\tau_{\kappa'} = 0$$

or in matrix notation

$$(\mathbf{K} - \theta\mathcal{I})\boldsymbol{\tau} = 0. \quad (24)$$

Therefore the Lagrangian multiplier must be a root of the secular determinant

$$\det(\mathbf{K} - \theta\mathcal{I}) = 0. \quad (25)$$

$K_{ij}$ is an exchange energy and $\theta$ is a function of these exchange energies. It is reasonable to interpret $\theta$ as an average exchange energy. There are $f^\alpha$ roots of Eq. (25) and hence $f^\alpha$ sets of mixing coefficients $\tau_\kappa$. For a given set of orbitals the lowest energy is achieved when $\theta$ has its lowest value. We say that the optimum mixed structure $|\Phi;\boldsymbol{\tau}\rangle$ is that set of mixing coefficients $\boldsymbol{\tau}$ which minimizes the average exchange energy.

Equations very similar to our SCF equations for structure kets also hold for matric basis projections[15] from $|\Phi\rangle$. We prefer the structure kets because (1) $\kappa$ is a simpler element than a matric basis element, (2) $\kappa$ corresponds to the bonding structures of chemistry, and (3) $\kappa$ generates the familiar Pauling numbers.

## SPIN-FREE SCF EQUATIONS FOR STRUCTURE KETS

Equation (22) expresses the energy of a mixed structure ket in terms of brackets between spin-free orbitals and the structure-mixing coefficients which are determined by Eqs. (24) and (25). The best spin-free orbitals will now be determined.

When the orbitals are subjected to the variations $|\delta\varphi_i\rangle$, the energy undergoes the variation

$$\delta E_\tau = \sum_i \langle \delta\varphi_i | M + \sum_j (J_j + T_{(ij)}K_j) | \varphi_i \rangle + \text{c.c.}$$

Here we have introduced the new operator $M$ defined by

$$M|\varphi_i\rangle \equiv h|\varphi_i\rangle - 2\langle\varphi_i|g|\varphi_i\varphi_i\rangle$$

and $J_j$, $K_j$ are defined as before. The variations are arbitrary except for the orthonormality condition, Eq. (11). Once again we introduce the Lagrangian multipliers $\epsilon_{ij}$ and find that the energy is minimized when

$$[M + \sum_j (J_j + T_{(ij)}K_j)]|\varphi_i\rangle = \sum_j \epsilon_{ij}|\varphi_j\rangle. \quad (26)$$

Equation (26) is the spin-free mixed structure Hartree-Fock equation.

## SOLUTION OF THE SPIN-FREE SCF EQUATIONS

The coupling between the spin-free SCF equations in the immanant case, Eq. (12), and the structure case, Eq. (26), is a complication which always appears in open-shell wave functions.[16] Various methods have been proposed to solve the coupled equations arising in the conventional formulation. Roothaan[2] was able to uncouple the equations by a suitable redefinition of the Fock operator. Lefebvre[17] proposed a perturbation approach which is applicable to the coupled equations. Both methods can be applied to the spin-free equations as we will now show.

For Roothaan's method it is necessary to examine in detail the transformation properties of the spin-free kets under transformations of the orbitals. Any nonsingular transformation, $A$, on the $N$ orbitals sends $|\Phi\rangle$ into $|\Phi_A\rangle$. The collection of all such transformations forms the general linear group in $N$ dimensions, $GL(N)$. As is well-known,[18] the irreducible subspaces of $\{|\Phi_A\rangle$, all $A\in GL(N)\}$ are precisely those which have been adapted to the symmetric group $S_N$. [Certain subgroups of $GL(N)$, such as the unitary group $U(N)$ and the special unitary group $SU(N)$ are also completely reduced by adaptation to $S_N$.] Hence a linear transformation of orbitals merely moves $|\Phi;\alpha\rangle$ and $|\Phi;\boldsymbol{\tau}\rangle$ through the space of all spin-free kets with permutational symmetry $\alpha$. This is equivalent to moving through the space of all different spin-coupling schemes with a given spin quantum number in the conventional formulation.

Roothaan's scheme is effective for a single structure. Without loss of generality we confine our attention to

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[15] W. A. Goddard, III, Phys. Rev. **157**, 73 (1967).

[16] In Goddard's method Ref. (15) of $G$ operators this difficulty is circumvented by relaxing the orthonormality condition among the orbitals. By requiring only that the orbitals remain normalized, the Lagrangian multipliers are automatically "diagonal." The resulting simplification is balanced by the complication introduced in the energy expression by nonorthogonal orbitals. Goddard's method may also be derived in the spin-free framework by removing the orthogonality of the orbitals from our immanant ket. His equations may also be generalized to mixed structures by corresponding changes in our structure kets.

[17] R. Lefebvre and C. M. Moser, J. Chim. Phys. **53**, 393 (1956).

[18] H. Boerner, *Representations of Groups* (North-Holland Publishing Co., Amsterdam, 1963).

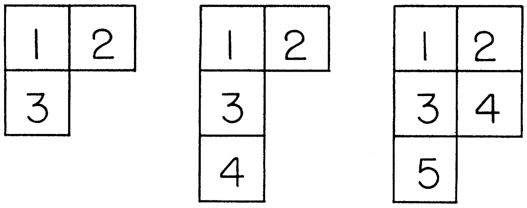

FIG. 1. First standard structures of three electrons in a doublet state, of four electrons in a triplet, and of five electrons in a doublet.

the "first" structure, $\kappa=I$ which is defined as follows. Let $T_I$ be the Young tableau of shape $\alpha=\{2^p,1^{N-2p}\}$, in which the integers 1, 2, $\cdots$ $N$ appear in the "lowest" order. That is, 1 and 2 lie in the first row, 3 and 4 in the second, $\cdots$ and 1, 3, 5, $\cdots$ lie in the first column. For example, the first structures of the permutation states $\{2,1\}$ for three electrons, $\{2,1,1\}$ for four electrons, and $\{2,2,1\}$ for five electrons are shown in Fig. 1. The row operator, $P$, of this tableau is the symmetrizer on rows: $P=(\mathscr{I}+(12))[\mathscr{I}+(34)]\cdots$. The column operator, $N$, of $T_I$ is the antisymmetrizer on columns: $N=[\mathscr{I}-(13)-(15)-(35)+(135)+(153)\cdots][\mathscr{I}-(24)\cdots]$. Then the structure projector is defined to be[19]

$$I=PN.$$

Two-columned tableaux such as those required for electrons divide the orbitals $\{|\varphi_1\rangle, |\varphi_2\rangle, \cdots |\varphi_N\rangle\}$ into two sets. Those which "belong" to the first column $\{|\varphi_1\rangle, |\varphi_3\rangle, \cdots\}$ and those which "belong" to the second $\{|\varphi_2\rangle, |\varphi_\kappa\rangle, \cdots\}$. Since $N$ consists of the product of the antisymmetrizers on these two sets it follows that

$$N|\Phi\rangle=\det\{|\varphi_1\rangle|\varphi_3\rangle\cdots\}\times\det\{|\varphi_2\rangle|\varphi_4\rangle\cdots\}.$$

Consider now a transformation $A$ which transforms orbitals of the first column among one another and orbitals of the second column among one another but does not transform between columns. For such a transformation it follows that

$$N|\Phi_A\rangle=(\det A)N|\Phi\rangle.$$

The structure ket $|\Phi,I\rangle$ then has the property

$$\begin{aligned}|\Phi_A,I\rangle&=PN|\Phi_A\rangle\\&=(\det A)PN|\Phi\rangle\\&=(\det A)|\Phi,I\rangle.\end{aligned}$$

In other words, $|\Phi,I\rangle$ is merely scaled by a linear transformation which does not mix orbitals of different columns. Hence the energy expression $E_I$ is left unchanged by such a transformation. Transformations of this kind can be used to diagonalize the $\epsilon$ matrix of Eq. (26) within the two blocks on the diagonal which pertain to the two columns of the tableau $T_I$. Roothaan's method will now be used to eliminate those $\epsilon$'s which mix orbitals between columns.

For the single structure $\kappa=I$, the coefficients $T_{(ij)}$ simplify to $(ij)_{II}$ since $\tau_I=1$. There are simple rules to compute these coefficients by group-theoretic methods.[5] The energy expression now becomes

$$\begin{aligned}&[M+\sum_j(J_j+(kj)_{II}K_j)]|\varphi_k\rangle\\&\qquad=\sum_l\epsilon_{lk}|\varphi_l\rangle+\sum_n\epsilon_{nk}|\varphi_n\rangle\end{aligned}\tag{27a}$$

and

$$\begin{aligned}&[M+\sum_j(J_j+(mj)_{II}K_j)]|\varphi_m\rangle\\&\qquad=\sum_l\epsilon_{lm}|\varphi_l\rangle+\sum_n\epsilon_{nm}|\varphi_n\rangle.\end{aligned}\tag{27b}$$

Here we have used the indices $k$, $l$ for orbitals of the first column and $m$, $n$ for the second while $i$, $j$ refer to orbitals from both sets.

From Eq. (27a) it follows that

$$\langle\varphi_m|M+\sum_j(J_j+(kj)_{II}K_j)|\varphi_k\rangle=\epsilon_{mk}.$$

Hence

$$\sum_m\epsilon_{mk}|\varphi_m\rangle=\sum_m|\varphi_m\rangle\langle\varphi_m|M+p\sum_j(J_j+(kj)_{II}K_j)|\varphi_k\rangle.$$

We define the new operator

$$E_1=1-\sum_m|\varphi_m\rangle\langle\varphi_m|.\tag{28}$$

Equation (27a) can now be written

$$E_1[M+\sum_j(J_j+(kj)_{II}K_j)]|\varphi_k\rangle=\sum_l\epsilon_{lk}|\varphi_l\rangle.\tag{29a}$$

Similarly, the orbitals of the first row can be transferred to the left side of Eq. (27b):

$$E_2[M+\sum_j(J_j+(mj)_{II}K_j)]|\varphi_m\rangle=\sum_n\epsilon_{nm}|\varphi_n\rangle,\tag{29b}$$

where

$$E_2=1-\sum_l|\varphi_l\rangle\langle\varphi_l|.\tag{30}$$

The diagonalization of columns may be applied to the two parts of Eq. (29) to convert them to eigenvalue-eigenket equations of the form

$$F_1|\varphi_k\rangle=\epsilon_k|\varphi_k\rangle\tag{31a}$$

and

$$F_2|\varphi_m\rangle=\epsilon_m|\varphi_m\rangle.\tag{31b}$$

We will not manipulate these equations any further though it might be convenient to derive a unified Fock operator so that orbitals of both columns are eigenkets of the same equation.

Next we take up the perturbation approach which we will apply to structure kets. It is easily modified for immanants. The energy expression for a mixed struc-

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[19] Matsen *et al.*, Ref. (5) chose the alternate definition, $I=NP$, because that choice leads to the Pauling numbers. The reverse order is the natural choice for examining the transformation properties of $|\Phi;\boldsymbol{\tau}\rangle$.

ture ket is [Eq. (22)].

$$E_\tau = \sum_i H_i + \tfrac{1}{2} \sum_{i\neq j} (J_{ij} + T_{(ij)} K_{ij}).$$

Now let the orbitals $\{|\varphi_1\rangle, |\varphi_2\rangle, \cdots, |\varphi_N\rangle\}$ be augmented to make a complete set $\{|\varphi_1\rangle, \cdots, |\varphi_N\rangle, |\varphi_{N+1}\rangle, \cdots\}$. A variation of $|\varphi_i\rangle$ may be written

$$|\varphi_i'\rangle = |\varphi_i\rangle + \sum_{k\neq i} c_{ik} |\varphi_k\rangle \tag{32}$$

with $c_{ik} = -c_{ki}$ (to preserve orthonormality—to first order). The new mixed structure ket constructed from these orbitals is

$$|\Phi'; \tau\rangle = |\Phi; \tau\rangle + \sum_{i=1}^{N} \sum_{k\neq i}^{\infty} c_{ik} |\Phi^{i,k}; \tau\rangle + \text{higher-order terms}. \tag{33}$$

Here $|\Phi^{i,k}; \tau\rangle \equiv \sum_\kappa \tau_{\kappa\kappa} |\Phi^{i,k}\rangle$ and $|\Phi^{i,k}\rangle$ differs from $|\Phi\rangle$ only in having $|\varphi_i\rangle$ replaced by $|\varphi_k\rangle$.

The corresponding change in energy is

$$\Delta E_\tau = \sum_{i=1}^{N} \sum_{k\neq i} c_{ik} \eta_{ik}, \tag{34}$$

where

$$\eta_{ik} = \langle \varphi_i | h | \varphi_k \rangle + \tfrac{1}{2} \sum_{j\neq i} (\langle \varphi_i \varphi_j | g | \varphi_k \varphi_j \rangle + T_{(ij)} \langle \varphi_i \varphi_j | g | \varphi_j \varphi_k \rangle).$$

The SCF orbitals are those for which $\eta_{ik} = 0$. If the initial orbitals $|\varphi_i\rangle$ are sufficiently close to the true SCF orbitals, they are improved by using the familiar perturbation coefficients:

$$c_{ik} = -\eta_{ik} / \eta_{kk} - \eta_{ii}. \tag{35}$$

Both Roothaan's separation technique and Lefebvre's perturbation method utilize an iterative method to find the SCF orbitals. From an initial guess of $|\varphi_i\rangle$ the Eqs. (31) or (35) are used to find improved orbitals. When the orbitals cease to change, the spin-free SCF orbitals have been achieved. These spin-free SCF orbitals are, of course, the same as the SCF orbitals which would arise in the conventional theory from pure spin components of a single-Slater determinant.

## DOUBLE OCCUPANCY

The Pauli principle for spin-free kets requires permutational symmetries of the restricted kind $\alpha = \{2^p, 1^{N-2p}\}$. It follows from this that if $|\Phi\rangle$ has more than two identical orbitals then

$$e^\alpha |\Phi\rangle = 0$$

and

$$\kappa |\Phi\rangle = 0.$$

Hence neither an immanant nor a structure function may be constructed with more than two electrons occupying the same orbital. Suppose there are $n (\leq \tfrac{1}{2} N)$ doubly occupied orbitals. Then we write

$$|\Phi\rangle = |\varphi_1\rangle |\varphi_1\rangle |\varphi_2\rangle |\varphi_2\rangle \cdots |\varphi_n\rangle |\varphi_n\rangle |\varphi_{2n+1}\rangle |\varphi_{2n+2}\rangle \cdots |\varphi_N\rangle. \tag{36}$$

The transpositions (12), (34), $\cdots$, $(2n-1, 2n)$ and all their products form a group which leaves $|\Phi\rangle$ invariant. This group of permutations is called the invariance subgroup of $|\Phi\rangle$ and is denoted by $S_\Phi$. The order of $S_\Phi$ is clearly $n_\Phi = 2^n$.

The left cosets of $S_\Phi$ in $S_N$ are denoted by $\{P_f S_\Phi, f = 1, 2, \cdots, n^\Phi\}$, where $n^\Phi$ is the index of $S_\Phi$ given by $n^\Phi n_\Phi = N!$ Two permutations $P_i$ and $P_j$ have the same effect on $|\Phi\rangle$ if and only if $P_i$ and $P_j$ belong to the same left coset:

$$P_i |\Phi\rangle = P_j |\Phi\rangle \Rightarrow P_j^{-1} P_i |\Phi\rangle = |\Phi\rangle. \tag{37}$$

That is $P_j^{-1} P_i \in S_\Phi$ or $P_i \in P_j S_\Phi$. The set of left coset generators $\{P_f, f = 1, 2, \cdots, n^\Phi\}$ brings about a unique expression for every permutation in terms of a $P_f$ and an element of $S_\Phi$. That is, if $P$ is any permutation there exists a unique pair $P_f$ and $S \in S_\Phi$ such that

$$P = P_f S.$$

Hence we can write the immanant as [see Eq. (3)]

$$|\Phi; \alpha\rangle = \frac{1}{\sqrt{N!}} \sum_f \chi_f^\alpha P_f |\Phi\rangle, \tag{38}$$

where $\chi_f^\alpha \equiv \sum_S \chi_{P_f S}^\alpha$ (the sum of characters of elements in the $P_f S_\Phi$ coset). The terms in the sum $\sum_f$ are distinct whereas those in $\sum_P$ are repeated. The normalization of $|\Phi; \alpha\rangle$ is now given by

$$\langle \Phi; \alpha | \Phi; \alpha \rangle = \frac{1}{f^\alpha} \sum_f \chi_f^\alpha \langle \Phi | P_f | \Phi \rangle. \tag{39}$$

Again we assume orthonormality of different orbitals so that $\langle \Phi | P_f | \Phi \rangle$ vanishes unless $P_f$ generates $S_\Phi$ i.e., $P_f$ leaves $|\Phi\rangle$ unchanged. Hence

$$\langle \Phi; \alpha | \Phi; \alpha \rangle = \chi_1^\alpha / f^\alpha,$$

where $\chi_1^\alpha$ is the sum of the characters of permutations which leave $|\Phi\rangle$ invariant.

The energy expression for an immanant wave function with doubly occupied orbitals becomes

$$\begin{aligned} E_\alpha &= \langle \Phi; \alpha | H | \Phi; \alpha \rangle / \langle \Phi; \alpha | \Phi; \alpha \rangle \\ &= \frac{1}{\chi_1^\alpha} [\sum_f \chi_f^\alpha \langle \Phi | H P_f | \Phi \rangle] \\ &= \sum_i \nu_i H_i + \sum_{ij} (\lambda_{ij} J_{ij} + \omega_{ij} K_{ij}), \end{aligned} \tag{40}$$

where

$\nu_1 = 2$ if $i \leq n$
$= 1$ if $i > n$, i.e., $\nu_i$ is the occupation number of the spinless orbital $|\varphi_i\rangle$. The numbers $\lambda_{ij}$ and $\omega_{ij}$ are derived in the Appendix.

In the special cases when $p=n$, i.e., the spin states $S=\frac{1}{2}(N-2n)$ there is only one structure, which is identical to the immanant. These spin-free kets correspond to single-Slater determinants in which the singly occupied orbitals are all given the same spin. For example, suppose $N=2n$, then $\nu_i=2$, $\lambda_{ij}=2$ (except for $j=i$ when $\lambda_{ii}=1$) and $\omega_{ij}=-1$ (except for $j=i$ when $\omega_{ii}=0$). Hence $E_\alpha$ becomes

$$E_\alpha=2\sum_i H_i+\sum_{ij}(2J_{ij}-K_{ij}), \tag{41}$$

which is the familiar result for a single-Slater determinant of doubly occupied orbitals.

The structure kets with double occupancy have norms:

$$\langle\Phi;\boldsymbol{\tau}|\Phi;\boldsymbol{\tau}\rangle=\sum_f T_f\langle\Phi|P|\Phi\rangle, \tag{42}$$

where $T_f\equiv\sum_s T_{P_fS}$. Again, orthonormality of orbitals allows only the single term to survive:

$$\langle\Phi;\boldsymbol{\tau}|\Phi;\boldsymbol{\tau}\rangle=T_1.$$

The energy expression becomes

$$\begin{aligned}E_\tau&=\frac{1}{T_1}\sum_f T_f\langle\Phi|HP_f|\Phi\rangle\\&=\sum_i \nu_iH_i+\sum_{ij}(\lambda_{ij}J_{ij}+\Omega_{ij}K_{ij}),\end{aligned} \tag{43}$$

where $\nu_i$ is the occupation number of the orbital $|\varphi_i\rangle$, $\Omega_{ij}$ is defined in the Appendix.

The HF equations for double occupancy now become, first for immanants:

$$[L'+\sum_j(\lambda_{ij}J_j+\omega_{ij}K_j)]|\varphi_i\rangle=\sum_j\epsilon_{ji}|\varphi_j\rangle, \tag{44}$$

where $L'$ is defined by

$$L'|\varphi_i\rangle=h|\varphi_i\rangle-(\lambda_{ii}+\omega_{ii})\langle\varphi_i|\nu|\varphi_i\varphi_i\rangle$$

and $J_j$ and $K_j$ are as before.

And second, for structure functions:

$$[M'+\sum_j(\lambda_{ij}J_j+\Omega_{ij}K_{ij})]|\varphi_i\rangle=\sum_j\epsilon_{ji}|\varphi_j\rangle. \tag{45}$$

Here $M'$ is defined by

$$M'|\varphi_i\rangle=h|\varphi_i\rangle-(\lambda_{ii}+\Omega_{ii})\langle\varphi_i|g|\varphi_i\varphi_i\rangle.$$

## SYMMETRY CONSIDERATIONS

Our spin-free SCF equations satisfy half of the requirements for the restricted Hartree-Fock method. Namely, they correspond to eigenkets of $S^2$. Spatial symmetry must be achieved separately as, for example, with Löwdin's $O_L$ projection operator.

Symmetry under the full rotation group (i.e., angular momentum) is of special interest. It often happens that adaptation with respect to $S_N$ simultaneously brings about pure rotational symmetry. For example, in the open-shell $p^4$ configuration[20] the permutation states with $\alpha=\{1^4\}$ and $\alpha=\{2,1^2\}$ are already eigenkets of $L^2$ and correspond to ${}^5S$ and ${}^3P$ states with no further projection. Similarly, an adaptation with respect to $S_N$ and the subgroup $C_\infty$ (i.e., $L_z$) may produce an eigenket of $L^2$ as happens for the ${}^1D$ state in the $p^4$ configuration.

Finite space-group symmetries can be treated by methods similar to that used for permutational symmetry.[21] Matric basis projectors can be used to give the desired symmetry and the appropriate energy expressions are easily derived. A complicating feature of such symmetries is the nonorthogonality of orbitals adapted to a space group. Nevertheless a form of SCF theory may be derived for such orbitals.[15]

## DISCUSSION

We have derived SCF equations for pure spin states of open-shell atoms and molecules. Spin was eliminated from the beginning in our derivation rather than being integrated away in the energy expression as in the conventional SCF theory. The spin-free approach removes the complexity of the double symmetry aspect—spin-permutational symmetry and space-permutational symmetry—which would be required to derive our equations by the conventional method.

States in which several structures are possible (spin-coupling schemes in the conventional vocabulary) are best described by a mixed structure. This mixing of structures is included in our formulation. For this purpose we defined an average exchange energy which is optimized to achieve the best mixture of structures. It is not necessary then to use the arbitrary mixture which results by projection with Löwdin's projection operator $O_S$. The spin-free equivalent of Löwdin's projected spin eigenket is the immanant for which we have also derived SCF equations. Immanants are appropriate for states with only one structure.

Open-shell kets are not only useful for atoms and molecules with partially filled shells. In another context they are often applied to what are usually thought of as closed-shell states. We refer to the different orbitals for different spins (DODS) scheme.[9] The merits of this method for molecular calculations have been discussed in relation to SCF theory by Goddard.[15] Open-shell (or DODS) spin-free kets provide smooth correlation between molecular states and separated atom states—hence giving improved dissociation limits over the conventional closed-shell kets.

Our results can be modified for use in nuclear calculations. Additional terms appear in the energy expression

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[20] F. A. Matsen, J. Phys. Chem. **70**, 1568 (1966).

[21] P. O. Löwdin, *Quantum Theory of Atoms, Molecules and the Solid State* (Academic Press Inc., New York, 1966).

when Bartlett, Heisenberg and Majorana potentials are introduced. More general permutational symmetries $\alpha=\{4^{p4},3^{p3},2^{p2},1^{p1}\}$ and tableaux with four columns must also be considered. Equations similar to our electron SCF equations may be derived for nucleons.

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## APPENDIX: DERIVATION OF $\nu_i$, $\lambda_{ij}$, $\omega_{ij}$, AND $\Omega_{ij}$

The energy of an immanant ket with double occupancy is [Eq. (40)]:

$$E_\alpha=\frac{1}{\chi_1{}^\alpha}\sum_f \chi_f{}^\alpha\langle\Phi|HP_f|\Phi\rangle,$$

where $P_f$ is the generator of a left coset of the invariance subgroup $S_\Phi$, and $\chi_f{}^\alpha$ is the sum of characters of permutations belonging to the $f$th coset. On substituting the form of the Hamiltonian, Eq. (7), into [Eq. (40)] we have

$$E_\alpha=\sum_i\frac{1}{\chi_1{}^\alpha}\sum_f \chi_f{}^\alpha\langle\Phi|h_iP_f|\Phi\rangle+\sum_{i<j}\frac{1}{\chi_1{}^\alpha}\sum_f\langle\Phi|g_{ij}P_f|\Phi\rangle.$$

The one-electron bracket $\langle\Phi|h_iP_f|\Phi\rangle$ vanishes unless $P_f|\Phi\rangle=|\Phi\rangle$, i.e., unless $P_f=\mathcal{I}$. Hence the first term becomes

$$\sum_i\langle\Phi|h_i|\Phi\rangle=\sum_i\langle\varphi_1\varphi_1\varphi_2\varphi_2\cdots\varphi_n\varphi_n\varphi_{2n+1}\cdots\varphi_N|h_i|\times\varphi_1\varphi_1\varphi_2\varphi_2\cdots\varphi_n\varphi_n\varphi_{2n+1}\cdots\varphi_N\rangle=\sum_{i=1}^N\nu_i\langle\varphi_i|h|\varphi_i\rangle,$$

where $\nu_i$ is the number of times $|\varphi_i\rangle$ appears in $|\Phi\rangle$. That is $\nu_i$ is the occupation number of the orbital $|\varphi_i\rangle$ and is given by

$$\nu_i=2,\ \text{if } i\leq n$$
$$=1,\ \text{if } 2n<i\leq N.$$

Two cosets give nonvanishing results for each $g_{ij}$. First, consider the identity coset generated by $P_f=\mathcal{I}$. For this coset

$$\begin{aligned}\sum_{i<j}\langle\Phi|g_{ij}|\Phi\rangle=&\sum_{i<j}\langle\varphi_1\varphi_1\cdots\varphi_n\varphi_n\varphi_{2n+1}\cdots\varphi_N|g_{ij}|\varphi_1\varphi_1\cdots\varphi_n\varphi_n\varphi_{2n+1}\cdots\varphi_N\rangle=\langle\varphi_1\varphi_1|g_{12}|\varphi_1\varphi_1\rangle+\langle\varphi_2\varphi_2|g_{34}|\varphi_2\varphi_2\rangle\\&+\cdots+\langle\varphi_n\varphi_n|g_{2n-1,2n}|\varphi_n\varphi_n\rangle+\langle\varphi_1\varphi_2|g_{13}+g_{23}+g_{14}+g_{24}|\varphi_1\varphi_2\rangle+\langle\varphi_1\varphi_3|g_{15}+g_{25}+g_{16}+g_{26}|\varphi_1\varphi_3\rangle+\cdots\\&+\langle\varphi_{n-1}\varphi_n|g_{2n-3,2n-1}+g_{2n-2,2n-2}+g_{2n-3,2n}+g_{2n-2,2n}|\varphi_{n-1}\varphi_n\rangle+\langle\varphi_1\varphi_{2n+1}|g_{1,2n+1}+g_{2,2n+1}|\varphi_1\varphi_{2n+1}\rangle+\cdots\\&+\langle\varphi_n\varphi_N|g_{2n-1,N}+g_{2n,n}|\varphi_n\varphi_N\rangle+\langle\varphi_{2n+1}\varphi_{2n+2}|g_{2n+1,2n+2}|\varphi_{2n+1}\varphi_{2n+2}\rangle+\cdots+\langle\varphi_{N-1}\varphi_N|g_{N-1,N}|\varphi_{N-1}\varphi_N\rangle\\&=\sum_{i=1}^n J_{ii}+4\sum_{i<j}^n J_{ij}+2\sum_{i=1}^n\sum_{j=2n+1}^N J_{ij}+\sum_{i=2n+1}^N\sum_{j>i}J_{ij}.\end{aligned}$$

More briefly,

$$\sum_{i<j}\langle\Phi|g_{ij}|\Phi\rangle=\sum_{i=1}^n J_{ii}+\sum_{i<j}\nu_i\nu_jJ_{ij}.$$

Finally, consider the remaining terms. These arise from cosets which permute pairs of distinct orbitals. For example,

$$\begin{aligned}&\langle\varphi_1\varphi_1\varphi_2\varphi_2\cdots\varphi_n\varphi_n\cdots\varphi_N|g_{13}|\varphi_2\varphi_1\varphi_1\varphi_2\cdots\varphi_n\varphi_n\cdots\varphi_N\rangle=\langle\varphi_1\varphi_2|g|\varphi_2\varphi_1\rangle=K_{12},\\&\langle\varphi_1\varphi_1\varphi_2\varphi_2\cdots\quad|g_{23}|\varphi_1\varphi_2\varphi_1\varphi_2\cdots\quad\rangle=K_{12},\\&\langle\varphi_1\varphi_1\varphi_2\varphi_2\cdots\quad|g_{14}|\varphi_2\varphi_1\varphi_2\varphi_1\cdots\quad\rangle=K_{12},\\&\langle\varphi_1\varphi_1\varphi_2\varphi_2\cdots\quad|g_{24}|\varphi_1\varphi_2\varphi_2\varphi_1\cdots\quad\rangle=K_{12},\end{aligned}$$

and

$$\begin{aligned}&\langle\varphi_1\varphi_1\varphi_2\varphi_2\cdots\varphi_n\varphi_n\varphi_{2n+1}\cdots\varphi_N|g_{1,2n+1}|\varphi_{2n+1}\varphi_1\varphi_2\varphi_2\cdots\varphi_n\varphi_n\varphi_1\cdots\varphi_N\rangle=K_{1,2n+1},\\&\langle\varphi_1\varphi_1\varphi_2\varphi_2\cdots\quad|g_{2,2n+1}|\varphi_1\varphi_{2n+1}\varphi_2\varphi_2\cdots\quad\rangle=K_{1,2n+1}\end{aligned}$$

and

$$\langle\varphi_1\varphi_1\cdots\varphi_n\varphi_n\varphi_{2n+1}\varphi_{2n+2}\cdots\varphi_N|g_{2n+1,2n+2}|\varphi_1\varphi_1\cdots\varphi_n\varphi_n\varphi_{2n+2}\varphi_{2n+1}\cdots\varphi_N\rangle=K_{2n+1,2n+2}.$$

The exchange bracket $K_{ij}$ appears $\nu_i\nu_j$ times $(i\neq j)$ with coefficients $\chi_{ij}{}^\alpha/\chi_1{}^\alpha$ where $\chi_{ij}{}^\alpha$ is the sum of characters of permutations in the coset which interchanges orbitals $|\varphi_i\rangle$ and $|\varphi_j\rangle$, there being $\nu_i\nu_j$ such cosets. Hence we have

$$E_\alpha=\sum_i\nu_i\langle\varphi_i|h|\varphi_j\rangle+\sum_{i\leq j}(\lambda_{ij}J_{ij}+\omega_{ij}K_{ij}),$$

where

$$\begin{aligned}\lambda_{ij}&=1,\ \text{if } i=j\leq n\\ &=0,\ \text{if } i=j>n\\ &=\nu_i\nu_j,\ \text{if } i\neq j\end{aligned}$$

and

$\omega_{ij}=$ (sum of characters of all permutations which interchange $|\varphi_i\rangle$ and $|\varphi_j\rangle$ in $|\Phi\rangle$)/ (sum of characters of all permutations which leave $|\Phi\rangle$ unchanged)

$=0$ if $i=j$.

The energy of a mixed structure ket is

$$E_\tau=\frac{1}{T_1}\sum_f T_f\langle\Phi|HP_f|\Phi\rangle,$$

where $T_f=\sum_S T_{P_fS}$; the sum on $S$ yielding the sum of all $T_P$ with $P$ a member of the $P_fS_\Phi$ coset. The same terms survive in this sum as in the case of immanants except with different coefficients. A derivation parallel to that for immanants gives

$$E_\tau=\sum_i \nu_i\langle\varphi_i|h|\varphi_i\rangle+\sum_{i\leqq j}(\lambda_{ij}J_{ij}+\Omega_{ij}K_{ij}),$$

where

$\Omega_{ij}=$ (sum of $T_p$ over all permutations which interchange the orbitals $|\varphi_i\rangle$ and $|\varphi_j\rangle$)/ (sum of $T_p$ over all permutations which leave $|\Phi\rangle$ unchanged).