

The Symmetric Group and the Spin Generalized SCF Method*

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Abstract

Some of the historical background for the development of the spin generalized self-consistent field methods is discussed. The important early work by Wigner, Weyl, Young, Heitler, Dirac, Serber, Yamanouchi and Kotani is emphasized.

In 1926, Wigner [1] considered approximating the wavefunction of an N electron system by using a linear combination of the $N!$ functions obtained from the product function

$$(1) \quad \Phi(1 \cdots N) = \phi_1(1)\phi_2(2) \cdots \phi_N(N)$$

by permuting the orbitals. Wigner pointed out that since the many-electron Hamiltonian, $\mathcal{H}(1 \cdots N)$, is invariant under permutations of the electrons, the exact (spatial) eigenfunctions, Ψ_i , can be taken as basis functions for the irreducible representations of the symmetric group, \mathcal{S}_N . Thus he showed that if the γ irreducible representation is of degree f^γ , the $N!$ degree secular equation can be reduced to an f^γ degree secular equation based on the matrix

$$(2) \quad H_{ij}^\gamma = \sum_{\tau \in \mathcal{S}_N} H_\tau U_{ij\tau}^\gamma$$

where U_τ^γ is the matrix representing τ in the γ irreducible representation and H_τ is the matrix element between product functions differing by τ ,

$$H_\tau = \langle \Phi | \mathcal{H} | \tau \Phi \rangle$$

The same approach was also used by Heitler [2], Dirac [3] and others [4], where assumptions concerning orthogonality of the orbitals in (1) were often made and few calculations were actually carried out.

* This paper is based on a discussion given at the 1969 International Symposium in honor of Henry Eyring, Sanibel Island, Florida.

† Alfred P. Sloan Fellow.

‡ Partially supported by a grant (GP-6965) from the National Science Foundation.

§ Contribution No. 3830.

The spin coordinates of the electrons were not included here because the Hamiltonian is taken to be independent of spin coordinates. Even so, the Pauli principle leads to an effective coupling between the spatial and spin parts of the wavefunction since the total wavefunction must be antisymmetric with respect to simultaneous permutation of the spatial-spin coordinates of the electrons. As discussed by Weyl [5] this leads to the requirement that the spatial and spin parts of the wavefunction transform as dual representations of \mathcal{S}_N . Weyl emphasized the convenience of Young tableaux [6] (or patterns) in describing the irreducible representations of \mathcal{S}_N and showed that dual representations correspond to transposed tableaux. For electrons the tableaux for the spin functions can have only one or two rows and thus the tableaux for the spatial functions can have only one or two columns. Thus although spin is not dynamically involved, through the Pauli principle it serves to determine the allowed spatial symmetry.

Dirac [3] made use of this duality to convert the $N!$ order secular equation, based on functions as in (1), into a smaller secular equation in terms of the spin representation. He then expressed the spin representation matrix elements in terms of spin operators. Van Vleck and many others [7] found this formalism quite convenient for discussing magnetism. In any case, the resulting secular equations can be reduced to the form (2) or its equivalent in terms of the dual spin representation, $U^{\bar{\gamma}}$,

$$(3) \quad H_{ij} = \sum_{\tau} \zeta_{\tau} H_{\tau} U_{ij}^{\bar{\gamma}}$$

where ζ_{τ} is the parity of τ .

In order to carry out calculations with (2), it is only necessary to evaluate the H_{τ} , determine the representation matrices U_{τ}^{γ} , and diagonalize the secular equation based on (2). Various approaches have been suggested for determining the U_{τ}^{γ} . Young derived general formulas for several representations conveniently related to the Young tableaux [6, 8] and Serber [4] suggested an alternative representation. Later Yamanouchi elegantly rederived Young's orthogonal representations from a consideration of the coupling of spin angular momenta [9].

Evaluating the H_{τ} was a more difficult job and only very approximate calculations were made in the 1930's. Even so the form (2) was considered in calculations by several workers including Serber [4], Yamanouchi [10], Kotani and Siga [11], Voge [12], and others. Often the orbitals of (1) were taken as orthogonal.

Besides energies, one also wishes to construct wavefunctions. Wigner [13] showed that functions belonging to the γ irreducible representation of the group can be constructed in terms of the matrices U_{τ}^{γ} as

$$(4) \quad \Phi_k^{\gamma} = O_{kj}^{\gamma} \Phi = \frac{f^{\gamma}}{g} \sum_{\tau} U_{jkr^{-1}(\tau\Phi)}^{\gamma}$$

where Φ is an arbitrary function, g is the order of the group and the O_{kj}^{γ} are called Wigner projection operators and have the following useful property:

$$(5) \quad O_{ij}^{\alpha} O_{kl}^{\beta} = \delta^{\alpha\beta} \delta_{jk} O_{il}^{\alpha}$$

Expression (4) for the wavefunctions was emphasized by Yamanouchi [9, 10] and Kotani [11]. Throughout much of this time workers using irreducible representations for \mathcal{S}_N dealt with many-electron spatial functions rather than functions with both spatial and spin coordinates. However, in 1955 Kotani and coworkers [14] wrote the total wavefunction as

$$(6) \quad \Phi_{S,M}(1 \cdots N) = \sum_{k=1}^{f^\gamma} \psi_{S,k}(1 \cdots N) \Theta_{S,M;k}(\sigma_1 \cdots \sigma_N)$$

where Ψ and Θ are functions of spatial and spin coordinates, respectively, and transform as dual irreducible representations of \mathcal{S}_N . This form of the wavefunction was used in several calculations by Kotani and co-workers [15]. In addition, Harris and Taylor [16] used functions of the form (6) based on several product functions Φ and allowed nonorthogonal orbitals for several systems with two, three, or four electrons.

As emphasized by Weyl, Young tableaux and Young operators [6] are convenient for discussions of the irreducible representations of \mathcal{S}_N . For N particles a tableau is a set of N boxes stacked in a specified way and containing the numbers 1 through N , such as

$$(7) \quad S_i^\gamma = \begin{array}{|c|c|c|c|} \hline 1 & 2 & 5 & 9 \\ \hline 3 & 6 & 8 & \\ \hline 4 & & & \\ \hline 7 & & & \\ \hline \end{array}$$

Young defined an operator P_i^γ which symmetrizes with respect to elements in the same rows of S_i^γ and another operator N_i^γ which antisymmetrizes with respect to elements in the same columns. These operators were combined into the Young operators

$$(8) \quad E_i^\gamma = P_i^\gamma N_i^\gamma$$

which could then be used to project a general function onto the space of functions transforming according to the γ irreducible representation. Using the functions (8) Young also developed the orthogonal units [6, 8],

$$(9) \quad \{O_{ij}^\gamma; i, j = 1, \cdots, f^\gamma\}$$

which are useful in constructing bases for irreducible representations of \mathcal{S}_N . These units transform according to the γ irreducible representations of \mathcal{S}_N and in fact are just Wigner projection operators for \mathcal{S}_N based on a specific representation, the Young's orthogonal representation.

Based on the work of Weyl and Wigner, Goddard [17] used Young's orthogonal units to construct the group operator

$$(10) \quad G_i^\gamma = \sum_{r=1}^{f^2} \zeta_{\sigma_{ri}} O_{ri}^\gamma \omega_{ri}^{\bar{\gamma}}$$

where O^γ and $\omega^{\bar{\gamma}}$ operate on spatial and spin coordinates, respectively and $\zeta_{\sigma_{ri}}$ is the parity of a permutation σ_{ri} associated with r and i . Here O^γ and $\omega^{\bar{\gamma}}$ are Young's orthogonal units based on the associated representations γ and $\bar{\gamma}$ and just correspond to Wigner projection operators for these representations. The group operator G_i^γ has the property that for any function of the spatial coordinates (say, Φ) and spin coordinates (say, χ),

$$G_i^\gamma \Phi \chi$$

is an eigenfunction of S^2 and satisfies Pauli's principle [17]. Taking a linear combination of the states of the same spin (i.e., same γ), we obtain

$$(11) \quad \sum_i C_i G_i^\gamma \Phi \chi$$

If the C_i in (11) are optimized, we obtain the best function which can be described in terms of Φ and permutations on Φ . If \mathcal{H} is the Hamiltonian the energy becomes

$$(12) \quad E = \frac{\sum_{ij} C_i^* C_j \langle \Phi | \mathcal{H} | O_{ij} \Phi \rangle}{\sum_{ij} C_i^* C_j \langle \Phi | O_{ij} \Phi \rangle}$$

after integrating over spin coordinates, and if we optimize the coefficients C_i we obtain

$$\sum_j \langle \Phi | \mathcal{H} | O_{ij} \Phi \rangle C_j = E \sum_j \langle \Phi | O_{ij} \Phi \rangle C_j$$

That is, the secular determinant becomes

$$(13) \quad \left\| \sum_\tau (H_\tau - S_\tau E) U_{i\tau} \right\| = 0$$

where

$$H_\tau = \langle \Phi | \mathcal{H} | \tau \Phi \rangle$$

$$S_\tau = \langle \Phi | \tau \Phi \rangle$$

This is just the secular determinant that Wigner [1] and Heitler [2] and Born [4] obtained (Wigner and Heitler assumed $S_\tau = \delta_{e,\tau}$). Although different in appearance the wavefunction in (11) is equivalent to Kotani's [14] as is the secular determinant (13).

It is simple to show [17] that the exact wavefunction can be written in the form (11)

$$(14) \quad \Psi^{\text{ex}} = \sum C_i G_i^\gamma \Phi^{\text{ex}} \chi$$

where Φ^{ex} is a suitable spatial function. Thus we may consider extensions of (11) in which Φ is replaced by a sum over several terms. However, for such configuration interaction calculations, it has been convenient to use linear combinations of Slater determinants [18] and avoid the complexity of calculating and combining the U_{ijr} .

Goddard has shown [17] that by redefining Φ^{ex} , the exact function can be written in terms of one group operator

$$(15) \quad \Phi^{\text{ex}} = G_i^\gamma \Phi^{\text{ex}} \chi$$

Thus we may legitimately consider sequences of improved wavefunctions converging on the exact wavefunction but involving only one group operator. In particular Goddard considered [19] an approximate form of (15)

$$(16) \quad G_i^\gamma \Phi^{\text{prod}} \chi$$

in which the spatial function is restricted to be a product of spatial orbitals

$$(17) \quad \Phi^{\text{prod}}(1, \dots, N) = \phi_1(1) \phi_2(2) \cdots \phi_N(N)$$

He then applied the variational condition that the orbitals lead to the best energy* and obtained the following equations for these optimum orbitals

$$(18) \quad H_k \phi_k = \varepsilon_k \phi_k \quad k = 1, \dots, N$$

where

$$(19) \quad H_k = h + U_k$$

h is the one particle operator in \mathcal{H} , and U_k involves integrations over the other $N - 1$ orbitals (excluding ϕ_k), see [19], Bibliography, for the detailed equations. Since Equations (18) lead to the best wavefunction of form (16) based on the i th group operator, G_i^γ , he called (18) the *GI* equations and the orbitals the *GI* orbitals; this emphasizes the fact that the optimum orbitals depend on which group operator, G_i , is used [19]. Equations (18), which must be solved self-consistently, have a form similar to the Hartree-Fock equations and may be solved in similar ways [20].

Goddard has shown [17] that the function

$$(20) \quad G_i^\gamma \Phi \chi$$

can be expressed as

$$(21) \quad G_i^\gamma \Phi \chi = f^{\gamma a} [\Phi(\omega_{ii} \chi)]$$

or

$$(22) \quad G_i^\gamma \Phi \chi = f^{\gamma a} [(O_{ii} \Phi) \chi]$$

* Actually the requirement was just that the energy be stationary. This usually leads to at least local minima in the energy.

Thus the function (20) can be viewed as a generalization of the Slater determinant in which the spin product χ is replaced by a spin eigenfunction, $\omega_{ii}\chi$, or alternatively we can view (20) as a Slater determinant in which the spatial function Φ is replaced by $O_{ii}\Phi$. The first viewpoint emphasizes the relation of the $G_i^{\gamma}\Phi\chi$ function to the i th spin coupling function, $\omega_{ii}\chi$, whereas the second emphasizes the total spatial symmetry resulting from the Pauli principle. In any case, if \mathcal{H} is independent of spin the use of (20) with (5) leads immediately to

$$(23) \quad E = \langle \Phi | \mathcal{H} | O_{ii}\Phi \rangle / \langle \Phi | O_{ii}\Phi \rangle$$

as the form for the total energy. That is, the spin terms are easily eliminated.

The definition of the Young's orthogonal units or Wigner projection operators in (4) depends upon the matrices of an irreducible representation. Thus these units could be changed by transforming to an equivalent representation. We used Young's orthogonal representation which has an advantage in that for all N , explicit formulas are known for the generators of \mathcal{S}_N [6, 8]. In addition, for this representation the important properties of the O_{ii} operator are made manifest by the form of the Young tableau. This representation has other additional advantages as discussed below. In fact we find that [21] the use of the first group operator leads to

$$(24) \quad G_1^{\gamma}\Phi\chi_1 = \text{const } a[(P_1\Phi)\chi_1] \\ = \text{const } a\{[(\phi_1(1)\phi_2(2) + \phi_2(1)\phi_1(2))(\phi_3(3)\phi_4(4) + \phi_4(3)\phi_3(4)) \cdots] \\ \times [\alpha(1)\beta(2)\alpha(3)\beta(4) \cdots]\}$$

and thus this function has the same form as a general valence bond function based on the normal bonding structure [22]. Normally in valence bond calculations the inner shell and nonbonding orbitals are doubly occupied (i.e., $\phi_{2j-1} = \phi_{2j}$) and the bonding orbitals are based on the atomic valence orbitals [22]. Since the $G1$ wavefunction corresponds to the best possible wavefunction of the form (24), the $G1$ wavefunction corresponds to a generalization of the valence bond wavefunction in which all double-occupation restrictions are removed, the orbitals are allowed to have a completely general form, and the orbitals are solved for self-consistency [23]. That is, the $G1$ method is a self-consistent-field generalization of the valence bond method [23].

In addition, if χ_f has $M_S = S$ we can write [17]

$$G_f\Phi\chi_f = \text{const } a[\Phi(\omega)_{ff}\chi_f] \\ = \text{const } a\left[\Phi\left(\sum_i \omega_{ii}\chi_f\right)\right] \\ = \text{const } a[\Phi(\mathcal{O}^S\chi_f)] \\ = \text{const } \mathcal{O}^S(a\Phi\chi_f)$$

where \mathcal{O}^S is the spin projection operator [17]

$$\mathcal{O}^S = \sum_i \omega_{ii}$$

and

$$\chi_f = \alpha(1)\alpha(2) \cdots \alpha(n)\beta(n+1) \cdots \beta(N)$$

Thus the $G_f\Phi\chi$ wavefunction is equivalent to a spin projected Slater determinant. This provides the connection between the GI method and Lowdin's extended Hartree-Fock (EHF) method [24]. If in EHF we apply just the spin projection operator, then the EHF wavefunction is equivalent to the GF wavefunction [19].

However, there is no special reason why we must restrict (4) to Young's orthogonal representation. In fact we should choose that representation which leads to the best possible wavefunction of the form (16). If the representations and orbitals are simultaneously optimized, the resulting equations have exactly the same form, (18), as the GI equations except that the new representation matrices are used in O_{ii} . For this reason we call this method the spin-coupling optimized GI (or $SOGI$) method [25].

Since the above types of self-consistent field (scf) methods are based on wavefunctions of the form (20) which have a more general form for the spin part of the wavefunction, we may refer to them as spin generalized scf methods. The major motivation behind these approaches has been to remove certain deficiencies of the Hartree-Fock method without sacrificing the interpretability of the wavefunction [19]. It appears from recent calculations using these methods on such systems as H_3 [26], BH [27], H_2O [28], CH_4 [29] and C_2H_2 [30] that the resulting wavefunctions do indeed allow conceptually useful interpretations.

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