SPIN-COUPLED WAVE FUNCTIONS FOR ATOMS AND MOLECULES

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Expressions are derived for matrix elements of the Hamiltonian operator for spin-coupled wave functions in molecular systems having an even number of electrons. Orthogonality of spatial orbitals is not assumed, and the coupling scheme can be specified at will. Relations to other methods are noted briefly.

An electronic wave function of the general form

$$\Psi_{S, M_S; k} = \sqrt{N!} \alpha (\Phi_s^N \Theta_s^N_{S, M_S; k})$$  \hfill (1)

is known as a spin-coupled wave function. In this expression, $\alpha$ is the usual antisymmetrizing projection operator, acting on both space and spin coordinates; the function $\Phi_s^N$ is a simple Hartree product of spatial orbitals

$$\Phi_s^N = \phi_1 (1) \phi_2 (2) \ldots \phi_N (N)$$  \hfill (2)

with $\langle \phi_\mu | \phi_\mu \rangle = 1$, $\mu = 1, 2, \ldots, N$,

and the function $\Theta_s^N_{S, M_S; k}$ is an $N$-electron spin function, the complete set of them forming a basis for an irreducible representation of the permutation group $S_N$. Thus for any permutation $P^\prime$ of the spin coordinates, we have

$$P^\prime \Theta_s^N_{S, M_S; k} = \epsilon_P \sum_{i=1}^{f_s^N} U_{ik}^{S}(P) \Theta_s^N_{S, M_S; i}$$  \hfill (3)

where $\epsilon_P = \pm 1$ is the parity of the permutation $P$ and $f_s^N$ is the dimension of the irreducible representation. The notation used by Kotani et al.\textsuperscript{1, 2} has been employed.

The functions $\Theta_s^N_{S, M_S; k}$ ($k = 1, 2, \ldots, f_s^N$) are orthonormal and hence are indeterminate to within an orthogonal transformation. If one chooses the basis so as to generate the Young-Yamanouchi\textsuperscript{3} irreducible representation, then the indices $k$ become the Yamanouchi symbols\textsuperscript{3} or, equivalently, the internal spin coupling indices of Kotani.\textsuperscript{1} In this case the $\Theta_s^N_{S, M_S; k}$ functions have the important property that the matrices $U(P)$ for $N - 1, N - 2, \ldots, 2$ particles appear in fully reduced form.

Although functions of the form (1) are a significant improvement over the conventional Hartree-Fock functions, and may be very important in the calculation and interpretation of such quantities as nuclear spin-spin coupling and other hyperfine interactions, very little progress has been made hitherto due to the difficulty of evaluating the matrix elements of the Hamiltonian. We wish here to report the results of some progress we have made with this problem; further details will be given in a lengthier communication.

Instead of choosing the standard Young-Yamanouchi basis in spin space, one may choose the following basis:

$$\chi_s^N_{S, M_S; k} = \sum_{M_{S_1}, M_{S_1}} \langle S_0 S_2 M_{S_1} M_{S_1} | S M_S \rangle \Theta_s^{N-M}_{S_1, M_{S_1}; k_1} \Theta_s^{M}_{S_2, M_{S_2}; k_2}$$

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where two Young-Yamanouchi functions of, respectively, \( N - M \) and \( M \) particles are coupled together to form a resultant, \( SM_s \) by means of the usual Clebsch-Gordan coefficient. In this basis, the matrices for both \( e_{N-M} \) and \( e_M \) appear in fully reduced form, the index \( k \) on the left-hand side now being understood to refer to a quartet of symbols \( \{ S_l S_k k_1 k_2 \} \). Using the basis (3), one may derive the following form for a function (1) in which the last \( M \) electrons are decoupled:

\[
\sqrt{\frac{M!(N-M)!}{N!}} \sum_{S'_l S'_k k'_1 k'_2 \atop S'_l S'_k k'_1 k'_2 \atop M'_l M'_k k'_1 k'_2} \langle S'_l S'_k | \Phi_{M'_l M'_k} | S M_s \rangle U_{s'_l s'_k k'_1 k'_2} = \phi(Q) \times \sqrt{(N-M)!} \alpha(\Phi_{N-M}^{N-M} | \Phi_{S_l S_k k_1 k_2}^M) = \sqrt{M!} \alpha(\Phi_{M}^{M} | \Phi_{S_l S_k k_1 k_2}^M) \}
\]

The permutations \( \bar{Q} \) in this expression are a set of \( N!/(N-M)!M! \) permutations that transfer orbitals between the functions \( \Phi_{N-M}^{N-M} \) and \( \Phi_{S_l S_k k_1 k_2}^{M} \), the bar on the symbol \( Q \) indicating that the permutations act on the orbitals \( \phi_{\alpha} \) and not on the electron coordinates. Expression (4) is essentially a rederivation of Jahn's result,4a and, in analogy with his work, one could term the quantities

\[
\sqrt{\frac{M!(N-M)!}{N!}} \langle S_l S_k S_M | S M_s \rangle U_{s_l s_k k_1 k_2} = \phi(Q) \times \sqrt{(N-M)!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) = \sqrt{M!} \alpha(\Phi_{M}^{M} | \Phi_{S_l S_k S_M}^M) \}
\]

"molecular coefficients of fractional parentage" (see also ref. 4b). Setting \( M \) equal to 1 or 2 in this last equation enables one to derive a formula for the expectation value of the total energy. Thus since

\[
\langle \sqrt{N!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) | \Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) \rangle = \langle \sqrt{N!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) | \Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) \rangle
\]

\[
= \langle \sqrt{N!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) | \sum_{i=1}^{N} h_i + \sum_{i>j=1}^{N} \theta_{ij} \rangle \sqrt{N!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) \rangle
\]

\[
= N \langle \sqrt{N!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) | h_N \rangle \sqrt{N!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) \rangle
\]

\[
+ \frac{1}{2} N(N-1) \langle \sqrt{N!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) | g_{N-1,N} \rangle \sqrt{N!} \alpha(\Phi_{N}^{N} | \Phi_{S_l S_k S_M}^M) \rangle
\]

we obtain eventually

\[
E = \sum_{QQ'} H_n(QQ'|Skk) \langle \phi_{\alpha} | h_N | \phi_{\alpha} \rangle + \sum_{Q_i Q_j} \sum_{Q_i' Q_j'} J_n(Q_i Q_j Q_i' Q_j'|Skk) \langle \phi_{\alpha} | g_{N-1,N} | \phi_{\alpha} \phi_{\alpha} \rangle
\]

\[
+ K_n(Q_i Q_j Q_i' Q_j'|Skk) \langle \phi_{\alpha} \phi_{\alpha} | g_{N-1,N} | \phi_{\alpha} \phi_{\alpha} \rangle \}
\]

(5)

The coefficients \( H_n \), \( J_n \), and \( K_n \) are given by

\[
H_n(QQ'|Skk) = \sum_{P\bar{S}\bar{N}} U_{kk}^S(Q^{-1}PQ) \langle \Phi_{N-1}^{N-1} | \Phi_{N-1}^{N-1} \rangle
\]

\[
J_n(Q_i Q_j Q_i' Q_j'|Skk) = \sum_{P\bar{k}\bar{N}} U_{kk}^S(Q^{-1}PQ) \langle \Phi_{N-2}^{N-2} | \Phi_{N-2}^{N-2} \rangle
\]

\[
K_n(Q_i Q_j Q_i' Q_j'|Skk) = \sum_{P\bar{S}\bar{N}} U_{kk}^S(P) \langle \Phi_{N}^{N} | \Phi_{N}^{N} \rangle
\]
In these formulae, \( \Phi^{N-1}(Q) \) denotes the first \( N - 1 \) orbitals of the configuration (2) with orbital \( \phi_Q \) replaced by \( \phi_N \), and similarly \( \Phi^{N-2}(Q') \) denotes an \( (N - 2) \)-electron configuration with orbitals \( \phi_{Q_1}, \phi_{Q_2} \) replaced by \( \phi_{N-1} \) and \( \phi_N \), respectively.

Note that formula (5) does not assume any orthogonality whatsoever among the orbitals, and depending upon which kinds of restrictions are placed upon the \( \phi_n \), equation (5) may be made to reduce to the energy expression for any of the orbital-type wave functions commonly used. Thus, if one specifies the \( \phi_n \) to be atomic orbitals, then (5) is the general valence-bond energy. Other commonly used approximations such as the Hartree-Fock, the AMO method of Löwdin and Pauncz, the NPSO method of Linnett, and the paired-electron function of Hurley, Lennard-Jones, and Pople may be embraced by imposing the following orthogonality restrictions:

\[
\langle \phi_\mu | \phi_v \rangle = \delta_{\mu-1, \nu}, \quad \mu = 2, 4, \ldots, N. \tag{41}\]

The \( H_n, J_n, \) and \( K_n \) coefficients may then be considerably simplified. Adopting a representation for the \( X_{SM,S;k} \) functions in which the permutations \( P_{2,4,\ldots} \) are diagonal (see ref. 4a), we obtain for the case \( N = \) even the following expression:

\[
E = \sum_{\mu=2,4,\ldots}^N \left[ (\mu|H_k^S|\mu) + (\mu|G_k^S|\mu) \right] + \sum_{\mu\nu=2,4,\ldots}^N \left[ (\nu|G_k^S|\nu) + U_{kk}^S(P_{\mu-1,\mu})(\mu|G_k^S|\nu) \right] + \sum_{\mu\nu=2,4,\ldots}^N \left[ U_{kk}^S(P_{\mu-1,\mu})(\mu|G_k^S|\nu) \right], \tag{9}\]

where the notation has been chosen to resemble that used in reference 7. Thus:

\[
(\mu|H_k^S|\mu) = \frac{1}{1 + U_{kk}^S(P_{\mu-1,\mu})\Delta_{\mu-1,\mu}} \left\{ \langle \phi_\mu | \delta | \phi_\mu \rangle + 2U_{kk}^S(P_{\mu-1,\mu})\Delta_{\mu-1,\mu} \right\}, \tag{5}\]

\[
(\mu|G_k^S|\mu) = \frac{1}{1 + U_{kk}^S(P_{\mu-1,\mu})\Delta_{\mu-1,\mu}} \times \left\{ \langle \phi_{\mu-1,\mu} | \phi_\mu | \phi_\mu \rangle + U_{kk}^S(P_{\mu-1,\mu})\delta_{\mu-1,\mu} \right\}, \tag{6}\]

\[
(\nu|G_k^S|\nu) = \frac{1}{1 + U_{kk}^S(P_{\mu-1,\mu})\Delta_{\mu-1,\mu}} \times \left\{ \langle \phi_{\nu-1,\mu} | \phi_{\nu-1,\mu} | \phi_\mu \rangle + U_{kk}^S(P_{\mu-1,\mu})\delta_{\nu-1,\mu} \right\}, \tag{7}\]

\[
(\nu|G_k^S|\nu) = \frac{1}{1 + U_{kk}^S(P_{\mu-1,\mu})\Delta_{\mu-1,\mu}} \times \left\{ \langle \phi_{\nu-1,\mu} | \phi_\mu | \phi_\mu \rangle + U_{kk}^S(P_{\mu-1,\mu})\delta_{\nu-1,\mu} \right\}, \tag{8}\]

\[
+ \langle \phi_{\nu-1,\mu} | \phi_\mu | \phi_\mu \rangle + 2U_{kk}^S(P_{\mu-1,\mu})\delta_{\mu-1,\mu} \right\}, \tag{9}\]

\[
+ \langle \phi_{\nu-1,\mu} | \phi_\mu | \phi_\mu \rangle + 2U_{kk}^S(P_{\mu-1,\mu})\delta_{\nu-1,\mu} \right\}, \tag{10}\]

\[
+ \langle \phi_{\nu-1,\mu} | \phi_\mu | \phi_\mu \rangle + 2U_{kk}^S(P_{\mu-1,\mu})\delta_{\nu-1,\mu} \right\}, \tag{11}\]
\[
(\mu\nu|G_{kk}^s|\nu\mu) = \frac{1}{1 + U_{kk}^s(P_{s-1,r})\Delta_{s-1,r}^2} \left\{ 1 + U_{kk}^s(P_{\mu-1,\mu})\Delta_{\mu-1,\mu}^2 \right\}
\]

\[
\times \left\{ (\phi_\mu \phi_\mu | g|\phi_\mu \phi_\mu| + (\phi_{\mu-1} \phi_{\mu-1}| g|\phi_\mu \phi_\mu| + (\phi_\mu \phi_{\mu-1}| g|\phi_\mu \phi_{\mu-1})
\right. \\
+ (\phi_{\mu-1} \phi_{\mu-1}| g|\phi_\mu \phi_{\mu-1}) + 2U_{kk}^s(P_{\mu-1,\mu})\Delta_{\mu-1,\mu}\{(\phi_\mu \phi_\mu | g|\phi_\mu \phi_\mu| + (\phi_{\mu-1} \phi_{\mu-1}| g|\phi_\mu \phi_{\mu-1})
\right. \\
+ (\phi_\mu \phi_{\mu-1}| g|\phi_\mu \phi_{\mu-1}) + 2U_{kk}^s(P_{\mu-1,\mu})U_{kk}^s(P_{s-1,r})\Delta_{\mu-1,\mu}\Delta_{s-1,r}
\right. \\
\times \left[ (\phi_\mu \phi_\mu | g|\phi_\mu \phi_{\mu-1}) + (\phi_{\mu-1} \phi_{\mu-1}| g|\phi_\mu \phi_{\mu-1}) \right] \right\}
\]

Upon choosing \( k \) to correspond to the spin-coupling case where each electron pair is first coupled to form a singlet, expression (9) immediately reduces to that of Hurley et al.\(^7\) Further restriction of the \( \phi_\mu \) so that each \( \phi_\mu \equiv \phi_{\mu-1} (\mu = 2, 4, \ldots N) \) then gives the usual MO expression. On the other hand, restriction of the \( \phi_\mu \)'s to the form \( a + kb \), where \( a \) and \( b \) are atomic orbitals, then yields the NPSO energy. The case of the AMO method is a little more complex as the \( \phi_\mu \) are ordered differently. This and other related matters will be considered in a later publication.

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