THE FREEON *N*-ELECTRON PROCEDURE
AND THE HUBBARD CONNECTION

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Abstract

The Hubbard connection correlates Hückel molecular orbital and valence bond states by means of the Hückel–Hubbard Hamiltonian. The connection is greatly simplified through the use of the freeon *N*-electron procedure. The present paper reviews the mathematical background for the procedure and shows how it applies to the Hubbard connection. The allyl radical is taken as an example.

1.   Introduction

The Hückel theory, while quite successful, has a number of serious deficiencies. It fails to predict

the observed number of states,

the observed separation between states,

the spin (multiplicity) quantum number, and

valence bond structures.

These errors are inherent in one-electron theory, but are corrected in *N*-electron theory, which takes into account the explicit electron repulsion and the permutational symmetry (indistinguishability) of the electrons. In this paper, we introduce electron repulsion by means of the Hückel–Hubbard Hamiltonian, whose electron correlation parameter (x) provides the Hubbard connection between molecular orbital and valence bond states. The Hubbard connection for the allyl radical is shown in fig. 1.
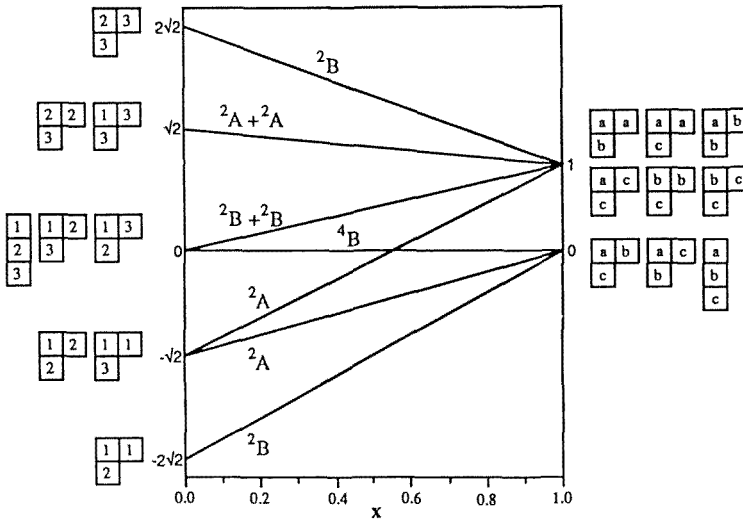
Fig. 1. The Hubbard connection for the allyl radical.

2. The state labeling

Electrons are identical, so the N-electron Hamiltonian must commute with the elements of the *symmetric group* S_N, the group of permutations on the electron indices. It follows that the S_N-irreducible spaces of the N-electron Hamiltonian are labeled by the S_N quantum number, a *partition* of N which is denoted

$$[\lambda] = [\lambda_1, \ldots, \lambda_i, \ldots, \lambda_N],$$

such that

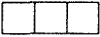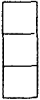$$\lambda_1 \geq \lambda_2 \geq, \ldots, \lambda_N \geq 0$$

and

$$\sum_i \lambda_i = N.$$

A partition $[\lambda]$ has a graphical realization as a *Young diagram*, denoted YD[λ], composed of an array of N boxes with λ_1 boxes in the first row, λ_2 boxes in the second row, etc. We denote by $Y(N)$ the number of Young diagrams for N electrons (see table 1).

Not all the states of the N-electron Hamiltonian are observed and these non-physical states are excluded by an *exclusion principle*. The *fermion exclusion principle* (the *Pauli antisymmetry principle*) classifies as physical only those states which are antisymmetric under the permutation of fermion orbital indices. These are states whose

Table 1

Partitions, Young diagrams, spins and multiplicities of the allyl system $(N = Y(N) = 3)$

$[\lambda]$	YD$[\lambda]$		S	M
$[3]$			Pauli excluded	
$[2, 1]$		$c_1 = 2, c_2 = 1)$	$\frac{1}{2}$	2 (doublet)
$[1^3]$		$c_1 = 3, c_2 = 0)$	$\frac{3}{2}$	4 (quartet)

Young diagram contains no more than one column. A fermion orbital is the tensor product of a *spin* orbital $|\sigma\rangle = |\alpha\rangle$ or $|\beta\rangle$ and a *freeon (spin-free) orbital*, $|v\rangle$, i.e.

$$|\omega\rangle = |v\rangle\,|\sigma\rangle.$$

For light atoms and in the absence of a magnetic field, the Hamiltonian is effectively spin-free, so the spin orbital is energetically inert. For a freeon (spin-free) Hamiltonian, we employ the *freeon N-electron procedure* with a *freeon exclusion principle*, which limits the physical states to those whose Young diagrams contain no more than two columns of lengths $c_1 \geq c_2 \geq 0$. For these freeon Young diagrams, the S_N quantum number translates into the spin and multiplicity quantum numbers as follows:

$$S = (c_1 - c_2)/2$$

and

$$M = c_1 - c_2 + 1.$$

The freeon N-electron procedure is simpler, conceptually, than the fermion procedure because it removes, for the uninitiated, the temptation to believe in spin–spin or magnetic interactions between the electrons.

3.   The symmetric group and its algebra [1]

The symmetric group is denoted

$$S_N\colon \{P_i, i = 1 \text{ to } N!\},$$

where P_i is a permutation on the electron indices of an N-electron wave function. For $N = 3$, the symmetric group is

$$S_3: \{I, (1, 2), (1, 3), (2, 3), (1, 2, 3), (1, 3, 2)\},$$

where $(1, 3, 2)$ exchanges electron 1 for electron 3, electron 3 for electron 2, and electron 2 for electron 1. The multiplication table for S_3 is

	I	$(1, 2)$	$(1, 3)$	$(2, 3)$	$(1, 2, 3)$	$(1, 3, 2)$
I	I	$(1, 2)$	$(1, 3)$	$(2, 3)$	$(1, 2, 3)$	$(1, 3, 2)$
$(1, 2)$	$(1, 2)$	I	$(1, 3, 2)$	$(1, 2, 3)$	$(2, 3)$	$(1, 3)$
$(1, 3)$	$(1, 3)$	$(1, 2, 3)$	I	$(1, 3, 2)$	$(1, 2)$	$(2, 3)$
$(2, 3)$	$(2, 3)$	$(1, 3, 2)$	$(1, 2, 3)$	I	$(1, 3)$	$(1, 2)$
$(1, 2, 3)$	$(1, 2, 3)$	$(2, 3)$	$(1, 2)$	$(1, 3)$	$(1, 3, 2)$	I
$(1, 3, 2)$	$(1, 3, 2)$	$(1, 3)$	$(2, 3)$	$(1, 2)$	I	$(1, 2, 3)$

The *Frobenius algebra* of S_N is an $N!$ dimension, operator, vector space spanned by the group elements:

$$FAS_N: \{P_i, i = 1 \text{ to } N!\},$$

with a general element

$$X = \sum_i X_i P_i, \; X_i \in \text{ complex field.}$$

Since group multiplication is associative, the Frobenius algebra is also associative. A second basis is the *Wigner basis*

$$FAS_N: \{e_{rs}^{[\lambda]}; [\lambda] = 1 \text{ to } Y(N); r, s = 1 \text{ to } f[\lambda]\}.$$

The basis operators are called *Wigner operators* and have the form

$$e_{rs}^{[\lambda]} = (1/f^{[\lambda]}) \sum_i [P_i^{-1}]_{sr}^{[\lambda]} P_i,$$

where $[P_i^{-1}]_{sr}^{[\lambda]}$ is the srth matrix element in the matrix representing P_i^{-1} in the $[\lambda]$th irreducible representation of S_N (see tables 2 and 3). The dimension of the $[\lambda]$th irreducible representation is

$$f^{[\lambda]} = N!/\pi \begin{array}{|c|c|} \hline h11 & h12 \\ \hline h21 & h22 \\ \hline h31 \\ \cline{1-1} \end{array},$$

Table 2

The irreducible representations and their character for S_3

	I	$(1, 2)$	$(1, 3)$	$(2, 3)$	$(1, 2, 3)$	$(1, 3, 2)$
⊞	$[1]$	$[1]$		$[1]$	$[1]$	$[1]$
⊟	$[1]$	$[-1]$	$[-1]$	$[-1]$	$[1]$	$[1]$
⊞	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$
χ	2	0	0	0	-1	-1

Table 3

The Wigner operators for S_3

$e_{11}^{\square\square\square} = (1/6)\,[I + (1, 2) + (1, 3) + (2, 3) + (1, 2, 3) + (1, 3, 2)]$

$e_{11} = (1/6)\,[I - (1, 2) - (1, 3) - (2, 3) + (1, 2, 3) + (1, 3, 2)]$

$e_{11} = (1/3)\,[I + (1, 2) - \tfrac{1}{2}[(1, 3) + (2, 3) + (1, 2, 3) + (1, 3, 2)]]$

$e_{12} = (1/3)\,(\sqrt{3}/2)\,[-(1, 3) + (2, 3) + (1, 2, 3) - (1, 3, 2)]$

$e_{21} = (1/3)\,(\sqrt{3}/2)\,[-(1, 3) + (2, 3) - (1, 2, 3) + (1, 3, 2)]$

$e_{22} = \tfrac{1}{3}[I - (1, 2) + \tfrac{1}{2}[(1, 3) + (2, 3) - (1, 2, 3) - (1, 3, 2)]]$

where hij is the number of squares traversed by an arrow drawn from the right through the ith row and hooking down through the jth column, and π denotes the product of the hij. For example:

$$f^{[2,1]} = 3!/\pi \quad \boxed{\begin{array}{cc} 3 & 1 \\ 1 \end{array}} \quad = 6/3 = 2.$$

The dimensionality statement for FAS_N is

$$N! = \sum_{[\lambda]} (f^{[\lambda]})^2.$$

The inverse transformation is

$$P_i = \sum_{[\lambda],r,s} [P_i]_{rs}^{[\lambda]} e_{rs}^{[\lambda]}.$$

The rule of multiplication of the Wigner operators is

$$e_{rs}^{[\lambda]} e_{r's'}^{[\lambda']} = \delta([\lambda],[\lambda]) \delta(s,r') e_{rs'}^{[\lambda]}.$$

Then

$$P_i \, e_{rs}^{[\lambda]} = \sum_{r'} [P_i]_{r's}^{[\lambda]} e_{r's}^{[\lambda]}$$

and

$$e_{rs}^{[\lambda]} P_i = \sum_{r'} [P_i]_{rs'}^{[\lambda]} e_{rs'}^{[\lambda]}.$$

4.   Symmetry adaption

Symmetry adaption is a basis transformation which factors the Hamiltonian matrix into blocks labeled by the S_N quantum number $[\lambda]$. We apply symmetry adaption to the basis of the Nth rank, n-freeon, orthonormal, orbital-product space,

$$V(n^N): \{|\Omega\rangle = |v_1\rangle |v_2\rangle, \ldots, |v_N\rangle\}$$

by means of Wigner operators. The symmetry-adapted vectors are called *Wigner states*:

$$|G;r\rangle \equiv |\Omega s; [\lambda]r\rangle \equiv N e_{rs}^{[\lambda]} |\Omega\rangle, \quad r = 1 \text{ to} f^{[\lambda]}.$$

Here, $G = \Omega s$ denotes a *Gel'fand tableau*; a useful mnemonic for the Wigner states which is taken from the theory of the unitary group $U(n)$ [2]. A tableau is constructed by adding the orbitals in $|\Omega\rangle$ to the Young diagram YD$[\lambda]$ in nondescending order along rows and ascending order down columns. Note that the number of rows in YD$[\lambda]$ cannot exceed n, the number of freeon orbitals. Further, since the freeon exclusion principle limits YD$[\lambda]$ to no more than two columns, no more than two electrons may be assigned to the same freeon orbital. All other states are said to be *Gel'fand excluded*. The number $f_n[\lambda]$ of Gel'fand tableaux which can be constructed from n orbitals and YD$[\lambda]$ is given by the following formula, due to Weyl:

$$f_n[\lambda] = \pi \begin{array}{|c|c|} \hline & n & n+1 \\ \hline n-1 & n \\ \hline n-2 & \\ \hline \end{array} \Big/ \pi \begin{array}{|c|c|} \hline h11 & h12 \\ \hline h21 & h22 \\ \hline h31 & \\ \hline \end{array}$$

The Pauli-allowed, atomic orbital Gel'fand tableaux for the allyl radical are listed in table 4.

Table 4

The Wigner states and their Gel'fand labeling for the allyl radical

The doublet states

$$YD[2,1] = \begin{array}{|c|c|} \hline & \\ \hline & \\ \hline \end{array} ; \quad f_3[2,1] = \pi \begin{array}{|c|c|} \hline 3 & 4 \\ \hline 2 & \\ \hline \end{array} \Big/ \pi \begin{array}{|c|c|} \hline 3 & 1 \\ \hline 1 & \\ \hline \end{array} = 24/3 = 8$$

$$\left\{ \begin{array}{|c|} \hline a \\ \hline b \\ \hline \end{array}\!\!\begin{array}{|c|} \hline a \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline a & a \\ \hline b & \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline a & b \\ \hline b & \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline a & b \\ \hline c & \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline a & c \\ \hline b & \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline a & c \\ \hline c & \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline b & b \\ \hline c & \\ \hline \end{array} \quad \begin{array}{|c|c|} \hline b & c \\ \hline c & \\ \hline \end{array} \right\}$$

The quartet state

$$YD[1^3] = \begin{array}{|c|} \hline \\ \hline \\ \hline \\ \hline \end{array} ; \quad f_3[1^3] = \pi \begin{array}{|c|} \hline 3 \\ \hline 2 \\ \hline 1 \\ \hline \end{array} \Big/ \pi \begin{array}{|c|} \hline 3 \\ \hline 2 \\ \hline 1 \\ \hline \end{array} = 6/6 = 1$$

$$\left\{ \begin{array}{|c|} \hline a \\ \hline b \\ \hline c \\ \hline \end{array} \right\}$$

Note that for $s = 2$ and double occupancy, the Wigner vectors vanish. These states are *Gel'fand forbidden*. To emphasize this, we give these zero states an illegal Gel'fand notation (see table 5).

5.   The S_N–Wigner–Eckart theorem

For an operator O on $V(v^N)$ such that

$$[O, P_i] = 0, \quad \forall\, P_i \in S_N,$$

Table 5

Wigner vectors for the allyl radical

$\left|\begin{smallmatrix} a & a \\ b & \end{smallmatrix}\,;1\right\rangle = \eta\,e_{11}^{\boxplus}|a_1\rangle|a_2\rangle|b_3\rangle = \tfrac{1}{\sqrt{6}}(2|a_1\rangle|a_2\rangle|b_3\rangle - |a_1\rangle|b_2\rangle|a_3\rangle - |b_1\rangle|a_2\rangle|a_3\rangle)$

$\left|\begin{smallmatrix} a & a \\ b & \end{smallmatrix}\,;2\right\rangle = \eta\,e_{21}^{\boxplus}|a_1\rangle|a_2\rangle|b_3\rangle = \tfrac{1}{\sqrt{2}}(|a_1\rangle|b_2\rangle|a_3\rangle - |b_1\rangle|a_2\rangle|a_3\rangle)$

$\left|\begin{smallmatrix} a & b \\ a & \end{smallmatrix}\,;1\right\rangle = \eta\,e_{12}^{\boxplus}|a_1\rangle|a_2\rangle|b_3\rangle = 0\ (\text{Gel'fand forbidden})$

$\left|\begin{smallmatrix} a & b \\ a & \end{smallmatrix}\,;2\right\rangle = \eta\,e_{22}^{\boxplus}|a_1\rangle|a_2\rangle|b_3\rangle = 0\ (\text{Gel'fand forbidden})$

$\left|\begin{smallmatrix} a & b \\ b & \end{smallmatrix}\,;1\right\rangle = \eta\,e_{11}^{\boxplus}|b_1\rangle|b_2\rangle|a_3\rangle = -\tfrac{1}{\sqrt{6}}(2|b_1\rangle|b_2\rangle|a_3\rangle - |a_1\rangle|b_2\rangle|b_3\rangle - |b_1\rangle|a_2\rangle|b_3\rangle)$

$\left|\begin{smallmatrix} a & b \\ b & \end{smallmatrix}\,;2\right\rangle = \eta\,e_{21}^{\boxplus}|b_1\rangle|b_2\rangle|a_3\rangle = \tfrac{1}{\sqrt{2}}(|b_1\rangle|a_2\rangle|b_3\rangle - |a_1\rangle|b_2\rangle|b_3\rangle)$

$\left|\begin{smallmatrix} b & a \\ b & \end{smallmatrix}\,;1\right\rangle = \eta\,e_{12}^{\boxplus}|b_1\rangle|b_2\rangle|a_3\rangle = 0\ (\text{Gel'fand forbidden})$

$\left|\begin{smallmatrix} b & a \\ b & \end{smallmatrix}\,;2\right\rangle = \eta\,e_{22}^{\boxplus}|b_1\rangle|b_2\rangle|a_3\rangle = 0\ (\text{Gel'fand forbidden})$

$\left|\begin{smallmatrix} a & b \\ c & \end{smallmatrix}\,;1\right\rangle = \eta\,e_{11}|a_1\rangle|b_2\rangle|c_3\rangle = \tfrac{1}{\sqrt{3}}(|a_1\rangle|b_2\rangle|c_3\rangle + |b_1\rangle|a_2\rangle|c_3\rangle$

$\qquad\qquad -\tfrac{1}{2}(|c_1\rangle|b_2\rangle|a_3\rangle + |a_1\rangle|c_2\rangle|b_3\rangle + |c_1\rangle|a_2\rangle|b_3\rangle + |b_1\rangle|c_2\rangle|a_3\rangle))$

$\left|\begin{smallmatrix} a & b \\ c & \end{smallmatrix}\,;2\right\rangle = \eta\,e_{21}|a_1\rangle|b_2\rangle|c_3\rangle$

$\qquad\qquad = \tfrac{1}{2}(-|c_1\rangle|b_2\rangle|a_3\rangle + |a_1\rangle|c_2\rangle|b_3\rangle - |c_1\rangle|a_2\rangle|b_3\rangle + |b_1\rangle|c_2\rangle|a_3\rangle)$

$\left|\begin{smallmatrix} a & c \\ b & \end{smallmatrix}\,;1\right\rangle = \eta\,e_{12}|a_1\rangle|b_2\rangle|c_3\rangle$

$\qquad\qquad = \tfrac{1}{2}(-|c_1\rangle|b_2\rangle|a_3\rangle + |a_1\rangle|c_2\rangle|b_3\rangle + |c_1\rangle|a_2\rangle|b_3\rangle + |b_1\rangle|c_2\rangle|a_3\rangle)$

$\left|\begin{smallmatrix} a & c \\ b & \end{smallmatrix}\,;2\right\rangle = \eta\,e_{22}|a_1\rangle|b_2\rangle|c_3\rangle$

$\qquad\qquad = \tfrac{1}{\sqrt{3}}(|a_1\rangle|b_2\rangle|c_3\rangle - |b_1\rangle|a_2\rangle|c_3\rangle$

$\qquad\qquad +\tfrac{1}{2}(|c_1\rangle|b_2\rangle|a_3\rangle + |a_1\rangle|c_2\rangle|b_3\rangle - |c_1\rangle|a_2\rangle|b_3\rangle - |b_1\rangle|c_2\rangle|a_3\rangle))$

etc.

the matrix elements over the Wigner states are given by

$$\langle G, [\lambda] r | O | G'; [\lambda'] r' \rangle = \delta([\lambda], [\lambda']) \, \delta(r, r') \langle G, [\lambda] \| O \| [\lambda] G' \rangle,$$

where

$$\langle G; [\lambda] \| O \| [\lambda] G' \rangle = N \, N'' \langle \Omega | O \, e_{ss'}^{[\lambda']} | \Omega' \rangle,$$

which follows directly from the rule of multiplication of the Wigner operators. We see that the matrix representation of O in $V(n^N)$ is factored into $Y(N)$ blocks labeled by $[\lambda]$ and that the $[\lambda]$th block is, in turn, factored into $f[\lambda]$ identical blocks.

The Wigner states are orthogonal ($O = I$). The orthogonality in r is explicit. If the orbitals in Ω and Ω' are different, the matrix element vanishes because of the orthogonality of the orbitals. If $\Omega = \Omega'$, the matrix element vanishes because only $e_{ss}^{[\lambda]}$ contain I or the Wigner states are Gel'fand forbidden.

For $O = H$, a freeon Hamiltonian, the eigenvalues with the $[\lambda]$ quantum number are $f^{[\lambda]}$-fold degenerate. This is a nonphysical degeneracy which is removed by the anti-symmetrization of products of freeon and spin spaces (see section 11).

6. The spin space

The Nth product spin space is denoted

$$V(2^N): \{ |\Sigma\rangle = |\sigma(N)\rangle = |\sigma_1\rangle |\sigma_2\rangle, \ldots, |\sigma_N\rangle, \quad \sigma = \alpha \text{ or } \beta \}.$$

Since there are only two spin orbitals, the spin YD$[\lambda^\sigma]$ contains no more than two rows. It is easy to show that the spin Wigner states are eigenvectors to S^2 and that invariant spaces are labeled by:

$$[\lambda^\sigma] = [N - S, S]$$

(see table 6). The spin Wigner states are constructed by means of the Wigner operator in the same way as the freeon Wigner states and are labeled $|G^\sigma[\lambda^\sigma]; r\rangle$.

7. Antisymmetrization

Antisymmetrization is the projection of N-electron fermion orbital product states which are antisymmetric under the permutation P^ω of the fermion orbital indices. The *antisymmetrizer is a projector* of the form

$$A = e^{[\lambda]}(1/N!) \sum_P (-1)^P P^\omega,$$

Table 6

The spin tableaux for S_N. Also listed are the S_z quantum numbers

Quartet state

YD[3,0] = (diagram)

$$\left\{ \boxed{\alpha\ \alpha\ \alpha}\quad \boxed{\alpha\ \alpha\ \beta}\quad \boxed{\alpha\ \beta\ \beta}\quad \boxed{\beta\ \beta\ \beta} \right\}$$

M_S 3/2   1/2   −1/2   −3/2

Doublet state

YD[2,1] = (diagram)

$$\left\{ \begin{array}{c}\boxed{\alpha\ \alpha}\\ \boxed{\beta}\end{array}\quad \begin{array}{c}\boxed{\alpha\ \beta}\\ \boxed{\beta}\end{array} \right\}$$

M_S 1/2   −1/2

where $[\lambda] = [1^N]$. Since we wish to apply the antisymmetrizer to a fermion space constructed from products of symmetry-adapted freeon and spin states, we write it in the form

$$A = (1/N!)\sum_P (-1)^P P^{\nu} \times P^{\sigma},$$

where P^{ν} and P^{σ} are permutations on the indices of freeon and spin orbitals, respectively. The antisymmetric vectors have the following form:

$$|G^{\nu}[\lambda]; G^{\sigma}[\lambda\ \ni]; [1^N]) = A\,|G^{\nu}[\lambda]\rho\rangle|G^{\sigma}[\lambda']t\rangle$$

$$= (1/N!)\sum_P (-1)^P P^{\nu}|G^{\nu}[\lambda]r\rangle P^{\sigma}|G^{\sigma}[\lambda']t\rangle$$

$$= (1/N!)\sum_{r't'}\sum_P (-1)^P [P]^{[\lambda]}_{r'r}[P]^{[\lambda]}_{t't}|G^{\nu}[\lambda]r'\rangle|G^{\sigma}[\lambda']t'\rangle$$

$$= \sum_{r't'}(1/N!)\left[\sum_P [P]^{[\lambda]^*}_{r'r}[P]^{[\lambda]}_{t't}\right]|G^{\nu}[\lambda]r'\rangle|G^{\sigma}[\lambda']t'\rangle,$$

where

$$[P]^{[\lambda]^*}_{r'r} = (-1)^P [P]^{[\lambda]}_{r'r}.$$

Here, $[\lambda]^*$ denotes the irreducible representation of S_N with is *conjugate* to $[\lambda]$. In YD$[\lambda]^*$, the rows and columns of YD$[\lambda]$ are interchanged. As a consequence of the irreducible representation orthogonality theorem:

$$[\,.\,.\,] = \delta([\lambda], [\lambda]^*)\,\delta(r, t)\,\delta(r', t')(N!/f^{[\lambda]}),$$

so the normalized antisymmetric vector is

$$|G^\nu[\lambda], G^\sigma[\lambda]^*; [1^N]\rangle = (1/f^{[\lambda]})^{1/2} \sum_r |G^\nu[\lambda]r\rangle\,|G^\sigma[\lambda]^*r\rangle.$$

The [2, 1] irreducible representation is self-conjugate; i.e [2, 1] = [2, 1]* and an anti-symmetrized vector is

$$|G^\nu[2, 1], G^\sigma[2, 1]^*; [1^N]\rangle = (1/2)^{1/2}\,|\,G^\nu[2, 1]1\rangle\,|G^\sigma[2, 1]2\rangle$$

$$+ |G^\nu[2, 1]2\rangle\,|G^\sigma[2, 1]1\rangle.$$

For example,

$$\boxed{\begin{array}{|c|c|}\hline a & a \\\hline b \\\cline{1-1}\end{array}}, \boxed{\begin{array}{|c|c|}\hline \alpha & \alpha \\\hline \beta \\\cline{1-1}\end{array}} ; [1^N]$$

$$= (1/2)^{1/2}(\tfrac{1}{\sqrt 6}(2|a_1\rangle|a_2\rangle|b_3\rangle - |a_1\rangle|b_2\rangle|a_3\rangle - |b_1\rangle|a_2\rangle|a_3\rangle))\tfrac{1}{\sqrt 2}(|\alpha_1\rangle|\beta_2\rangle|\alpha_3\rangle$$

$$- |\beta_1\rangle|\alpha_2\rangle|\alpha_3\rangle)) + (1/2)^{1/2}\tfrac{1}{\sqrt 2}(|a_1\rangle|b_2\rangle|a_3\rangle - |b_1\rangle|a_2\rangle|a_3\rangle))\tfrac{1}{\sqrt 6}(2|\alpha_1\rangle|\alpha_2\rangle|\beta_3\rangle$$

$$- |\alpha_1\rangle|\beta_2\rangle|\alpha_3\rangle - |\beta_1\rangle|\alpha_2\rangle|\alpha_3\rangle)).$$

The matrix element of the freeon Hamiltonian over a pair of normalized antisymmetric vectors is then

$$\langle G^n, [\lambda]; G^\sigma[\lambda]^*|H|\,G^{\nu}; [\lambda'], G^\sigma[\lambda']^*; [1^N]\rangle$$

$$= (1/f^{[\lambda]})\sum_{rr'}\langle G^\nu[\lambda]r|H|\langle G^\nu \ni, [\lambda']r'\rangle\langle G^\sigma[\lambda]^*r|G^\sigma[\lambda']^*r'\rangle$$

$$= \delta([\lambda], [\lambda']^*)\delta(r, r')(1/f^{[\lambda]})\sum_r\langle G^\nu[\lambda]r|H|G^{\nu}[\lambda]r\rangle$$

$$\equiv \delta([\lambda], [\lambda'])\langle G^\nu[\lambda]||H||G^{\nu}[\lambda]\rangle.$$

We see that antisymmetrization removes the degeneracy inherent in the freeon formation and that the freeon eigenvalues are obtained by diagonalizing the reduced matrix-element representation of the freeon Hamiltonian.

8.   The ketbra Hamiltonian

THEOREM

Any freeon Hamiltonian can be put in the following form:

$$H = \sum_r h_{rs}(E_{rs} + E_{sr}) - (1/2) \sum_{r,s,t,u} v_{rs,tu}(E_{rs}E_{tu} - \delta(s,t)E_{ru}),$$

where

$$E_{rs} = \sum_{n=1}^{N} |r_i\rangle\langle s_i|.$$

Proof

We write the Schrödinger Hamiltonian in the following form:

$$H = H^0 + V.$$

Here,

$$H^0 = \sum_i h_i,$$

where h_i is a general one-electron Hamiltonian and

$$V = \sum_{i<j} e^2/r_{ij}.$$

The matrix elements of the Schrödinger Hamiltonian in $V(n^N)$ are duplicated with the following ketbra realization:

$$H^0 = \sum_{i=1}^{N} \sum_{r,s=1}^{n} |r_i\rangle h_{rs}\langle s_i|$$

and

$$V = \sum_{i<j} \sum_{r,s,t,u=1}^{n} |t_j\rangle|r_i\rangle v_{rs,tu}\langle s_i|\langle u_j| = \sum_{r,s,t,u=1}^{n} v_{rs,tu} W_{rs,tu},$$

where the parameters h_{rs} and $v_{rs,tu}$ are defined as follows:

$$h_{rs} = \langle r_i|h_i|s_i\rangle$$

and

$$v_{rs,tu} = \langle t_j|\langle r_i|g_{rs}|s_i\rangle|u_j\rangle.$$

Both parameters are independent of the electron indices i and j because electrons are identical. In terms of the E_{rs}, we have

$$H^0 = \sum_{r,s=1}^{n} h_{rs} E_{rs} \,.$$

To express V, we rewrite $W_{rs,tu}$ as follows:

$$W_{rs,tu} = \sum_{i<j} |t_j\rangle |r_i\rangle \langle s_i| \langle u_j| = \sum_{i<j} (|r_i\rangle \langle s_i|)(|t_j\rangle \langle u_j|)$$

$$= \tfrac{1}{2} \sum_{i \neq j} (|r_i\rangle \langle s_i|)(|t_j\rangle \langle u_j|)$$

$$= \tfrac{1}{2} \sum_{i,j}^{N} (|r_i\rangle \langle s_i|)(|t_j\rangle \langle u_j|) - \sum_{i=1}^{N} (|r_i\rangle \langle s_i|)(|t_i\rangle \langle u_i|),$$

where we have added and subtracted terms for $i = j$. Now,

$$\langle s_i|t_i\rangle = \delta(s,t),$$

independent of i, so

$$W_{rs,tu} = \tfrac{1}{2} \sum_{i,j}^{N} (|r_i\rangle \langle s_i|)(|t_j\rangle \langle u_j|) - \delta(s,t) \sum_{i=1}^{N} |r_i\rangle \langle u_i|$$

$$= \tfrac{1}{2}(E_{rs} E_{tu} - \delta(s,t) E_{ru}). \qquad \qquad \square$$

To obtain the eigenvalues and eigenvectors of the Hamiltonian, we compute the Hamiltonian matrix in a symmetry-adapted basis of multiplicity M spanned by Wigner states:

$$[H] = [\langle G|H|G'\rangle],$$

where

$$\langle G|H|G'\rangle = \sum_{r,s} h_{rs} \langle G|E_{rs}|G'\rangle + \tfrac{1}{2} \sum_{r,s,t,u} v_{rs,tu} \langle G|(E_{rs}E_{tu} - \delta(s,t)E_{ru})|G'\rangle.$$

This form of the Hamiltonian is called the "freeon unitary group" Hamiltonian because E_{rs} are the infinitesimal generators of the unitary group $U(n)$, where n is the number of the freeon orbitals. This Hamiltonian is the basis of the freeon unitary group formulation of the N-electron theory. The irreducible spaces of $U(n)$ are also labeled by partitions of N, the same freeon exclusion principle applies, and state labeling applies.

The basis vectors are labeled by Gel'fand tableaux and are generated algebraically from the highest-weight state [2] and the Hamiltonian matrix elements evaluated algebraically.

In some formulations of the unitary group procedure, the $U(n)$ generators are expressed in second-quantized form as follows:

$$E_{rs} = a_{r\alpha}^\dagger a_{s\alpha} + a_{r\beta}^\dagger a_{s\beta}.$$

We prefer to keep spin out of the freeon formulation.

9.   The Hückel–Hubbard theory

The *Hückel–Hubbard theory* employs the following orbital space:

$$V_n : \{|r\rangle,\ r = 1 \text{ to } n\},$$

where n is the number of atomic sites in the π system and the Hamiltonian

$$H = (x - 1) \sum_{\langle rs \rangle} (E_{rs} + E_{sr}) + x \, \tfrac{1}{2} \sum_r (E_{rr}^2 - E_{rr}).$$

The *correlation parameter* (x) is defined by

$$0 \le x \equiv U/(U + t) \le 1,$$

where t is the negative of the Hückel β and (the Hubbard) U is the electron repulsion parameter for two electrons on a single site. For $x = 1$, the atomic orbital Gel'fand states are eigenvectors to the Hamilttonian with eigenvalues

$$E(1) = d,$$

where d is the number of doubly occupied atomic orbitals (see fig. 1).

The Hückel–Hubbard Hamiltonian can also be expressed in terms of molecular orbitals. The expansion of the atomic orbitals in terms of molecular orbitals is given by the Hückel theory:

$$|r\rangle = \sum_k |k\rangle \langle k | r\rangle.$$

Furthermore,

$$h_{kl} = \langle k_i | h_i | l_i \rangle = \delta(k, l) \varepsilon_k (x - 1)$$

and

$$v_{kl,mn} = \langle m_j | \langle k_i | g_{ij} | l_i \rangle | n_j \rangle = \sum_{r,s,t,u} \langle t_j | \langle r_i | g_{ij} | s_i \rangle | u_j \rangle \langle m_j | t_j \rangle \langle k_i | r_i \rangle \langle s_i | l_i \rangle \langle u_j | n_j \rangle.$$

Now,

$$\langle t_j | \langle r_i | g_{ij} | s_i \rangle | u_j \rangle = \delta(r, s, t, u) x,$$

so

$$v_{kl,mn} = x \sum_r \langle m | r \rangle \langle k | r \rangle \langle r | l \rangle \langle s | l \rangle,$$

so

$$H = (x - 1) \sum_k e_k E_{kk} + x \frac{1}{2} \sum_{kl,mn} v_{kl,mn} (E_{kl} E_{mn} - \delta(s,t) E_{kn}).$$

For $x = 0$, the molecular orbital Gel'fand states are eigenvectors to the Hückel–Hubbard Hamiltonian with eigenvalues

$$E(0) = \sum_k w_k \varepsilon_k ,$$

where ε_k is the energy of the kth molecular orbital and w_k is the occupation number of the kth molecular orbital. For the allyl radical, the molecular orbital energies in reduced units are $-\sqrt{2}$, 0 and $+\sqrt{2}$ (see fig. 1).

The spectrum for intermediate values of x can be computed from the Wigner states and the ketbra form of the generators, or by means of the unitary group algebra.

10. The linear Hückel–Hubbard spectrum

We have legitimized and explicated the freeon N-electron procedure and have applied it to the Hückel–Hubbard theory of the allyl radical. We now note that in many cases, including the allyl radical, the Hubbard connection can be made without detailed calculation by a linear interpolation scheme, which proceeds as follows.

(1) Plot and label with appropriate Gel'fand tableaux the molecular orbital eigenvalues at $x = 0$ and the atomic orbital eigenvalues at $x = 1$.

(2) Connect the molecular orbital states with the atomic orbital states in order of increasing energy with the same multiplicity and point group symmetry.

(3) Observe the no-crossing rule for states of the same multiplicity and point group symmetry.

We take the minimum point group of the allyl radical to be C_2. The point group symmetry of the MO Gel'fand states ($x = 0$) is A or B if the occupancy of $|2\rangle$ is even or odd, respectively. The degenerate ground atomic states ($x = 1$) combine to form an A state and a B state (see below). This is sufficient to draw the linear correlation diagram shown in fig. 1.

11. The valence bond states

Our final task is to construct valence bond states from our freeon atomic Wigner states. We define a valence bond state $|a - b, c - d, \ldots\rangle$ as a state in which bonded-orbital pairs are invariant under the exchange of the orbitals in the pairs; thus,

$$P_{ab} P_{cd} \ldots |a - c, c - d, \ldots\rangle = |a - c, c - d, \ldots\rangle.$$

To construct these vectors, we require the transformation properties of the Wigner states under orbital permutations:

$$P_{ab}^0 |G\rangle = N e_{rs}^{[\lambda]} P_{ab}^0 |\Omega\rangle$$

$$= N e_{rs}^{[\lambda]} (P_{12}^e)^{-1} |\Omega\rangle$$

$$= \sum_{s'} [P_{12}]_{rs'}^{[\lambda]} N e_{rs'}^{[\lambda]} |\Omega\rangle$$

$$= \sum_{s'} [P_{12}]_{rs'}^{[\lambda]} |G'\rangle.$$

Consequently, the transformation properties of the Wigner states can be determined from the irreducible representations of S_N (see table 7).

Table 7

The transformation properties of the Wigner doublet states for $N = 3$

	$\begin{array}{cc}a&b\\c\end{array}$	$\begin{array}{cc}a&c\\b\end{array}$
P_{ab}	$\begin{array}{cc}a&b\\c\end{array}$	$-\begin{array}{cc}a&c\\b\end{array}$
P_{bc}	$-(1/\sqrt{2})\begin{array}{cc}a&b\\c\end{array} \quad +(\sqrt{3}/2)\begin{array}{cc}a&c\\b\end{array}$	$(\sqrt{3}/2)\begin{array}{cc}a&b\\c\end{array} \quad +(1/\sqrt{2})\begin{array}{cc}a&c\\b\end{array}$
P_{ac}	$-(1/\sqrt{2})\begin{array}{cc}a&b\\c\end{array} \quad -(\sqrt{3}/2)\begin{array}{cc}a&c\\b\end{array}$	$-(\sqrt{3}/2)\begin{array}{cc}a&b\\c\end{array} \quad -(1/\sqrt{2})\begin{array}{cc}a&c\\b\end{array}$

The valence bond states for the allyl radical are listed in table 8. We note that the three valence bond states are linearly dependent. This is an example of

Table 8

Valence bond states

$$|C=C-\overset{\bullet}{C}\rangle = \begin{array}{|c|c|} \hline a & b \\ \hline c \\ \cline{1-1} \end{array}$$

$$|\overset{\bullet}{C}-C=C\rangle = \tfrac{1}{2}\begin{array}{|c|c|} \hline a & b \\ \hline c \\ \cline{1-1} \end{array} + \tfrac{\sqrt{3}}{2}\begin{array}{|c|c|} \hline a & c \\ \hline b \\ \cline{1-1} \end{array}$$

$$|C-\overset{\bullet}{C}-C\rangle = \tfrac{1}{2}\begin{array}{|c|c|} \hline a & b \\ \hline c \\ \cline{1-1} \end{array} - \tfrac{\sqrt{3}}{2}\begin{array}{|c|c|} \hline a & c \\ \hline b \\ \cline{1-1} \end{array}$$

Rumer's rule for the linear dependence of valence bond states. The C_2 symmetry-adapted covalent states are

$$|^2B\rangle = |C=C-\overset{\bullet}{C}\rangle + |\overset{\bullet}{C}-C=C\rangle,$$

$$|^2A\rangle = |C-\overset{\bullet}{C}-C\rangle,$$

which are antisymmetric and symmetric, respectively, under P_{ac} and are good approximations to the two lowest energy eigenvectors for x close to one. The ground state $|^2B\rangle$ is called a *resonating valence bond state* (RVB). Anderson has used such states in his RVB theory of superconductivity. He describes the different structure as differing in the flipping of spins and the interaction between the structures as magnetic. These concepts do not occur in the freeon formulation.

The unpaired electron density of the central allyl radical atom (b) has been estimated to be $\rho_b = -0.16$. At $x = 0$, $|2\rangle$ is assigned the unpaired electron, but it has an electron density of zero on the central atom; so at $x = 0$, $\rho_b = 0$, while for $x \approx 1$, $\rho_b = -1/3$, so the experimental value of x is ≈ 0.5. In practice, the molecular orbital states ($x = 0$) give the best approximation of the spectrum and the valence bond states ($x \approx 1$) give the best approximation to the structure.

12. Summary and conclusions

We have presented the theoretical basis of the freeon N-electron procedure and applied the procedure together with the Hückel–Hubbard Hamiltonian to produce the Hubbard connection between molecular orbital and valence bond states. Further details of the Hubbard connections are to be found in the soon-to-be-published Pariser–Parr–Pople volume of the International Journal of Quantum Chemistry.

References

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