Introduction to Various General Aspects of *Ab Initio* VB Theory

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Synopsis

- Properties of the ‘exact’ electronic wavefunction
- Examples of matrix element calculations & of a simple VB approach
- Spin eigenfunctions: Kotani, Serber, Rumer

Properties of the 'Exact' Electronic Wavefunction

Consider 'exact' *N*-electron wavefunctions $\Psi_{SM}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \sigma_1, \ldots, \sigma_N)$:

$\hat{\mathrm{H}}\Psi_{SM} = E\Psi_{SM}$	spin-independent, clamped-nuclei $\hat{\mathrm{H}}$
$\hat{\mathrm{S}}^2\Psi_{SM} = S(S+1)\Psi_{SM}$ $\hat{\mathrm{S}}_z\Psi_{SM} = M_S\Psi_{SM}$	$\hat{\mathrm{H}}$ commutes with $\hat{\mathrm{S}}^2$ and $\hat{\mathrm{S}}_z$
$\mathrm{P}\Psi_{SM} = \epsilon_{\mathrm{P}}\Psi_{SM}$ $\forall\ \mathrm{P} \in \mathcal{S}_N$	ϵ_{P}: parity of permutation $\mathrm{P} = \mathrm{P}^{\mathrm{r}}\mathrm{P}^{\sigma} = \mathrm{P}^{\sigma}\mathrm{P}^{\mathrm{r}}$ $\mathcal{S}_N$: symmetric group of degree *N*
$[\hat{\mathrm{H}}, \mathrm{P}^{\mathrm{r}}] = 0$	$\hat{\mathrm{H}}$ is completely symmetric under all permutations P^{r}

Eigenfunctions of $\hat{\mathrm{H}}$ can be chosen to form bases for irreducible representations ("irreps") of $\mathcal{S}_N$

Wigner's fullest possible space-spin factorization of **exact** solution:

$$\Psi_{SM}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \sigma_1, \ldots, \sigma_N) = (f_S^N)^{-½} \sum_k^{f_S^N} \Phi_{Sk}^N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \Theta_{SM;k}^N(\sigma_1, \ldots, \sigma_N)$$

Spin eigenfunctions $\Theta_{SM;k}^N$.

Spatial functions Φ_{Sk}^N (can be taken to be orthonormal) form a basis for an irrep of $\mathcal{S}_N$.

f_S^N is dimension of the irrep:

$$f_S^N = \binom{N}{½N + S} - \binom{N}{½N + S + 1} = \frac{(2S+1)N!}{(½N + S + 1)!\,(½N - S)!}$$

$$\sum_{S=0 \text{ or } ½}^{½N} (2S+1)\, f_S^N = 2^N$$

Orthonormal spatial functions Φ_{Sk}^{N} form a basis for an irrep of $\mathcal{S}_N$ of dimension f_S^N:

$$\mathrm{P}^{\mathrm{r}}\Phi_{Sk}^{N} = \sum_{l}^{f_S^N} U_{lk}^{SN}(\mathrm{P})\Phi_{Sl}^{N}$$

Representation matrices $\mathbf{U}^{SN}(\mathrm{P})$

Spin eigenfunctions $\Theta_{SM;k}^{N}$ could also be chosen to be orthogonal:

$$\mathrm{P}^{\sigma}\Theta_{SM;k}^{N} = \epsilon_{\mathrm{P}} \sum_{l}^{f_S^N} U_{lk}^{SN}(\mathrm{P})\Theta_{SM;k}^{N}$$

Representation matrices $\epsilon_{\mathrm{P}}\mathbf{U}^{SN}(\mathrm{P})$

("dual" or "conjugate" irrep)

Consider instead $\Phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ – still **exact** but no particular permutational symmetry:

$$\Psi_{SM;k}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \sigma_1, \ldots, \sigma_N) = (N!)^{½}\, \mathcal{A}\left(\Phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\Theta^N_{SM;k}(\sigma_1, \ldots, \sigma_N)\right)$$

$$\Psi_{SM}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \sigma_1, \ldots, \sigma_N) = \sum_k^{f_S^N} c_{Sk}\, \Psi_{SM;k}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \sigma_1, \ldots, \sigma_N)$$

$$\mathcal{A} = \frac{1}{N!} \sum_{\mathrm{P} \in \mathcal{S}_N} \epsilon_{\mathrm{P}} \mathrm{P}^{\mathrm{r}} \mathrm{P}^{\sigma}$$

(idempotent) antisymmetrizing operator $\mathcal{A}$

$$\Phi^N_{Sl} = \sum_k^{f_S^N} c_{Sk}\, \omega^S_{lk} \Phi$$

$$\omega^S_{lk} = (f_S^N/N!)^{½} \sum_{\mathrm{P} \in \mathcal{S}_N} U^{SN}_{lk}(\mathrm{P})\, \mathrm{P}^{\mathrm{r}}$$

projection operator ω^S_{lk}

Calculation of Matrix Elements

Matrix element of (spin-independent) operator $\hat{\mathrm{X}}$:

$$X_{kl} = \left\langle \Psi_{SM;k} \middle| \hat{\mathrm{X}} \middle| \Psi_{SM;l} \right\rangle = N! \left\langle \mathcal{A}\left(\Phi\Theta^{N}_{SM;k}\right) \middle| \hat{\mathrm{X}} \middle| \mathcal{A}\left(\Phi\Theta^{N}_{SM;l}\right) \right\rangle = \sum_{\mathrm{P}\in\mathcal{S}_N} U^{SN}_{lk}(\mathrm{P}) \left\langle \mathrm{P}^{\mathrm{r}}\Phi \middle| \hat{\mathrm{X}} \middle| \Phi \right\rangle$$

Range of strategies to alleviate the "*N*! problem".

Example: Direct Use of the Löwdin formula

Slater determinants U and V built up from nonorthogonal spin-orbitals u_i and v_j for a system of n_α and n_β electrons ($N = n_\alpha + n_\beta$):

$$\langle U|V\rangle = D_{UV} = D^{\alpha}_{UV} D^{\beta}_{UV}$$

$$\langle U|\hat{H}_1|V\rangle = \sum_{i\ j}^{N} \langle u_i|\hat{\mathrm{H}}_1|v_j\rangle\, D_{UV}(i|j) = D^{\beta}_{UV} \sum_{i\ ,j}^{n_\alpha} \langle u_i|\hat{\mathrm{H}}_1|v_j\rangle\, D^{\alpha}_{UV}(i|j) + D^{\alpha}_{UV} \sum_{i,j}^{n_\beta} \langle u_i|\hat{\mathrm{H}}_1|v_j\rangle\, D^{\beta}_{UV}(i|j)$$

etc

D_{UV} is determinant of overlap matrix (elements $\langle u_i|v_j\rangle$).

$D_{UV}(i|j)$ and $D_{UV}(ij|kl)$ are cofactors of order N–1 and N–2.

- Same determinant U could appear in multiple VB structures
- Same cofactor of order (say) $n_\alpha - 2$ could occur for different U, V pairs
- Laplace expansion – *e.g.*

$$D_{UV}(i|j) = \sum_{k}^{N} \langle u_m | v_k \rangle D_{UV}(im|jk)$$

Other approaches: permanents, $\mathbf{U}^{SN}(\mathrm{P})$ matrices, specific forms of ω_{lk}^{S}, …

☞ Second quantization!

Example of a simple VB approach: VBSCF

Generalized Brillouin theorem: $\langle \Psi_0 \vert \hat{\mathrm{H}} - E_0 \vert \Psi_{ij} \rangle = 0$	Ψ_{ij} corresponds to replacing u_i whenever it occurs in reference function Ψ_0 by u_j
Orbital mixing: $u_i \rightarrow b_0 u_i + \sum_j b_{ij} u_j$	corresponding to 1st order (small changes): $\Psi_0 \rightarrow \Psi_0 + \frac{1}{b_0} \sum_{ij} b_{ij} \Psi_{ij}$
Coefficients can actually be determined by minimizing energy of $\Psi_{\mathrm{BI}} = b_0 \Psi_0 + \sum_{ij} b_{ij} \Psi_{ij}$	summation over all linearly independent excitations that can change the energy

Basic recipe:

- Choose starting orbitals and list of VB structures.
- Solve secular equations → first Ψ_0
- Minimize energy of Ψ_{BI} → updated orbitals → new Ψ_0
- Iterate until $b_0 \approx 1$ and all $b_{ij} \approx 0$

More modern methods typically use 2nd derivative matrix (Hessian):

→ switch to Newton-Raphson-type schemes

→ convergence in fewer iterations

Spin Eigenfunctions

$$\hat{\mathrm{S}}^2\Psi_{SM} = S(S+1)\Psi_{SM}$$

$$\hat{\mathrm{S}}_z\Psi_{SM} = M_S\Psi_{SM}$$

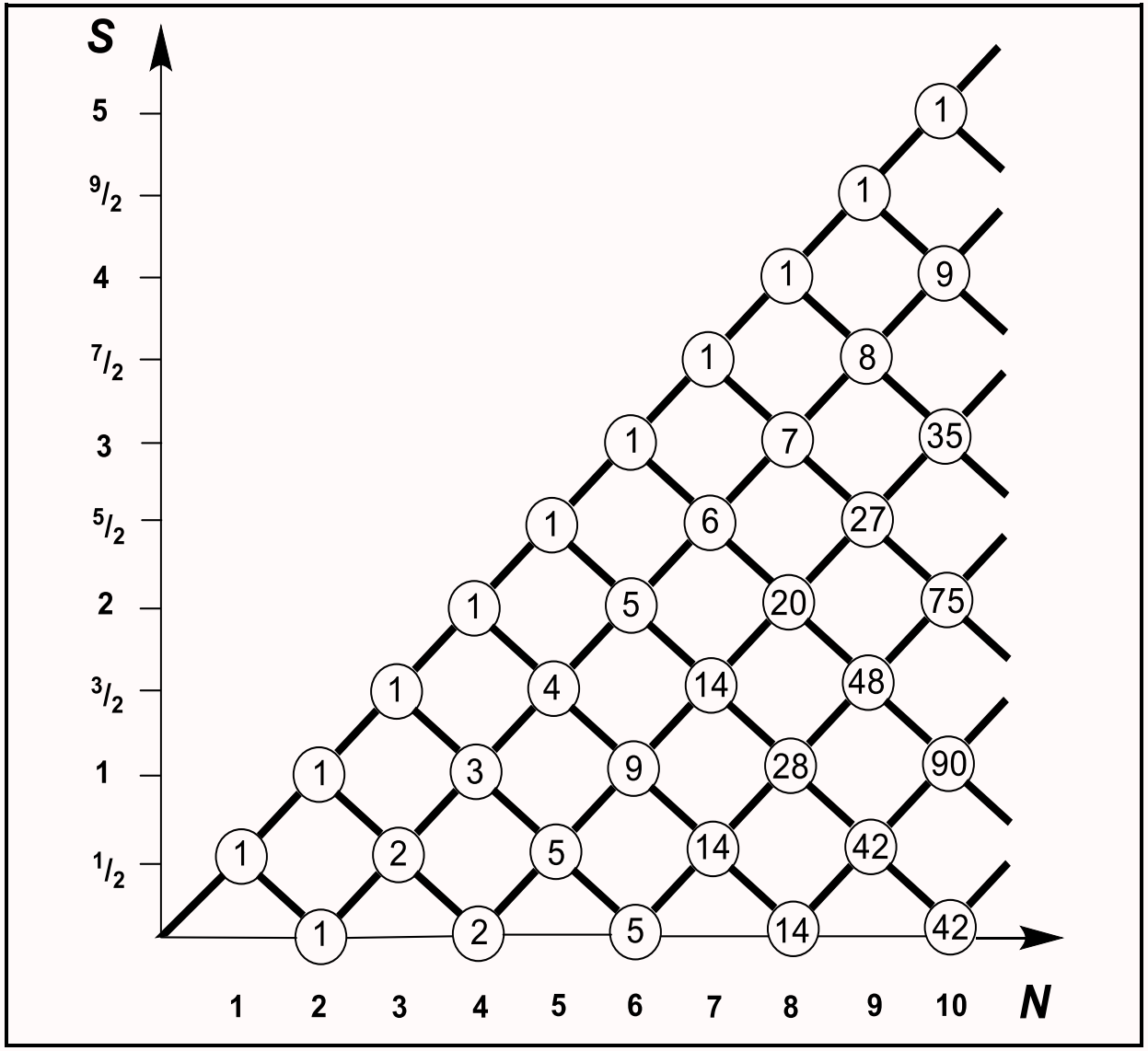
$\hat{\mathrm{H}}$ commutes with $\hat{\mathrm{S}}^2$ and $\hat{\mathrm{S}}_z$

- Kotani
- Serber
- Rumer

"I could have done it in a much more complicated way," said the Red Queen, immensely proud.

Kotani Spin Functions

- 'Standard genealogical' functions: branching diagram (Kotani) and Young standard tableau (Young-Yamanouchi) schemes are equivalent.
- Electron spins are coupled one at a time according to standard rules for coupling angular momenta, such that each partial spin function is an eigenfunction of $\hat{\mathrm{S}}^2$.
- Each $\Theta^N_{SM;k}$ corresponds to a vector of $N-1$ partial spin functions; there are f^N_S ways to construct such a vector, which can be conveniently visualized as rightwards path through a branching diagram.
- Ordering convention: from the right, highest path is first, next highest is second, … lowest path is last.
- $\mathbf{U}^{SN}(\mathrm{P})$ matrices are fully reduced on passing down subgroups $\mathcal{S}_{N-1}$, $\mathcal{S}_{N-2}$, …, $\mathcal{S}_1$.



$f_S^N = f_{S+½}^{N-1} + f_{S-½}^{N-1}$

(for $S \geq ½$)

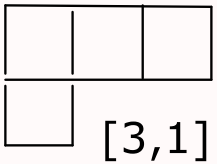
f_S^N increases rather rapidly for larger N

Every irrep of $\mathcal{S}_N$ is characterized by a particular partition of *N*.

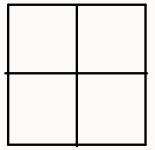
$\mathcal{S}_4$: [4], [3,1], [2^2], [2, 1^2] and [1^4]

→ Young frames

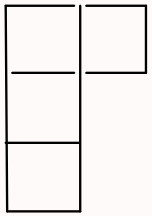
[4]



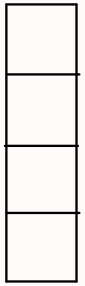
[3,1]



[2^2]



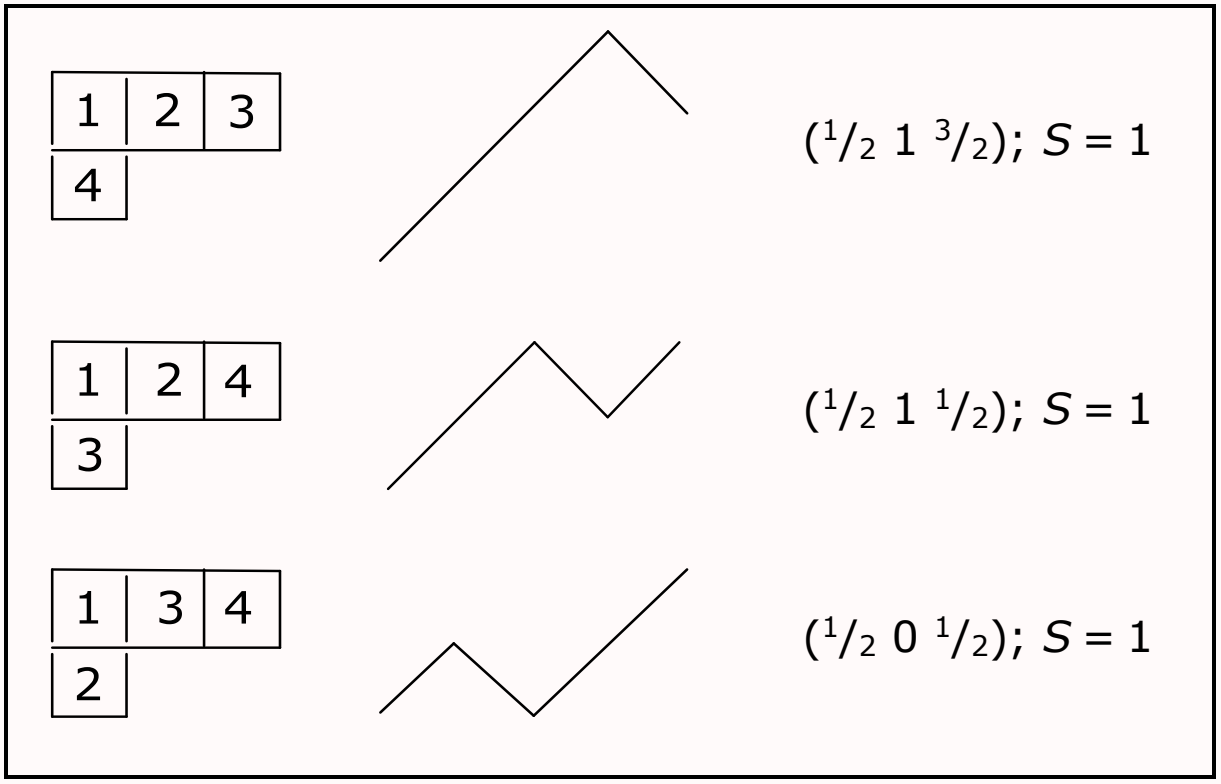
[2,1^2]



[1^4]

Partitions corresponding to spin functions for electrons cannot contain more than two rows (& corresponding spatial representations cannot have more than two columns).

Young standard tableaux: distribute integers 1,2,…,*N* into the cells so that they increase along any row and down any column:



Mapping: from $i-1$ to i, add upwards segment if i in upper row (otherwise downwards)

Serber Spin Functions

Useful (but less often used) alternative to Kotani.

Built from both singlet and triplet pairs of electrons, combined sequentially according to standard rules for coupling angular momenta.

Does not correspond to a standard representation of $\mathcal{S}_N$ (but simple diagonal **U** matrices for $P_{\mu-1,\mu}$ transpositions).

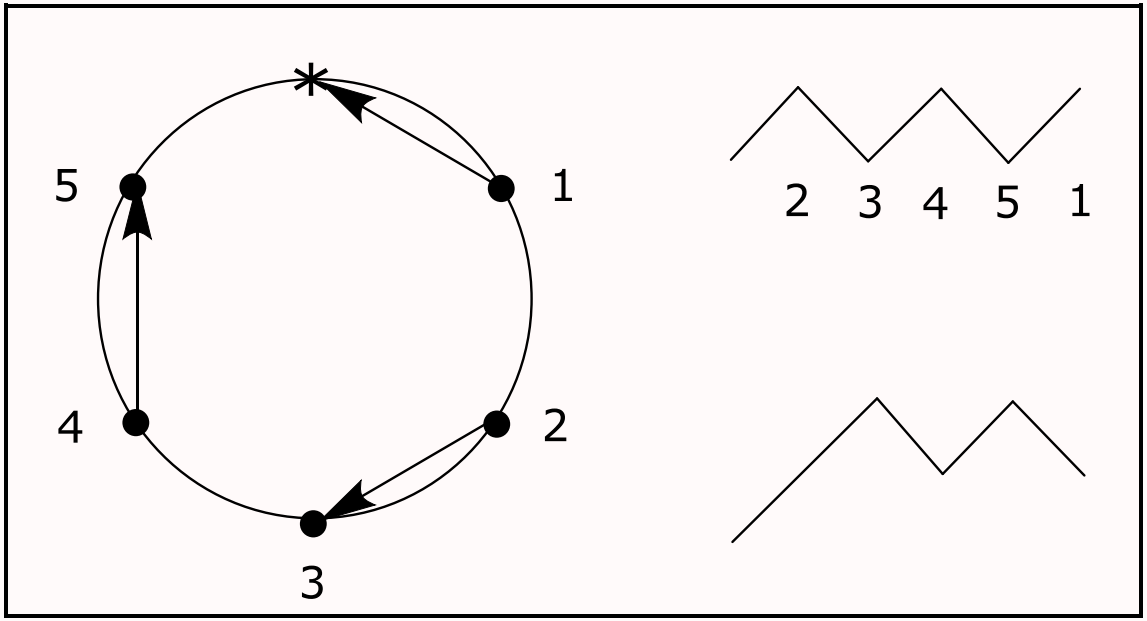
Rumer Spin Functions

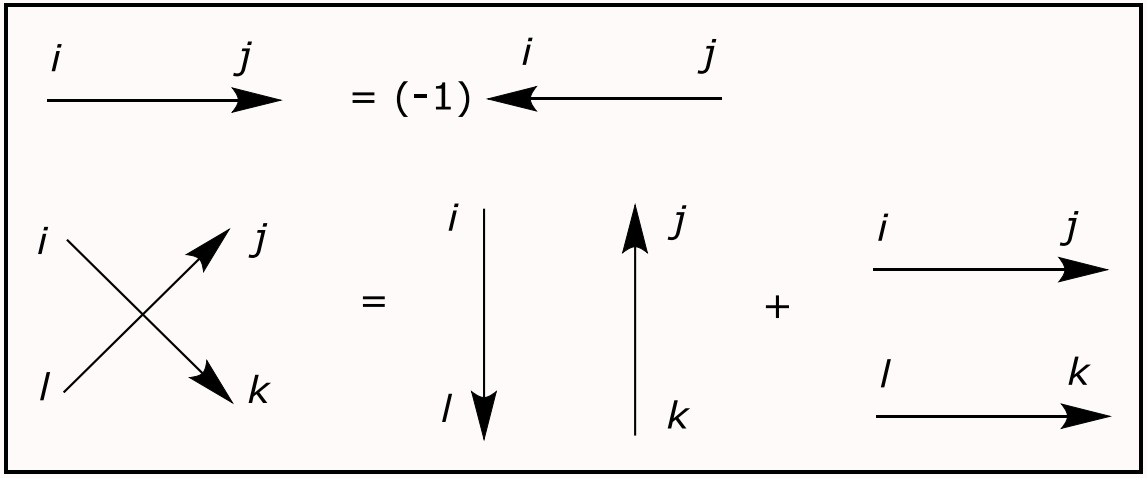
- Often easy to link to bonding models – maximum pairing of electron spins.
- Basic units: singlet electron pairs (and 2*S* unpaired spins).
- Can generate a full set of f_S^N linearly independent Rumer functions in various ways.
- Such Rumer functions are nonorthogonal.

Extended Rumer diagram:

- Number *N* points clockwise on a circle, starting next to the pole.
- Link 2*S* points to the pole.
- Link the remaining *N*−2*S* points in pairs: no two connections can cross.
- $k \longrightarrow l\ (k < l)\ \Rightarrow [\alpha(k)\beta(l) - \beta(k)\alpha(l)]/\sqrt{2}$ and $r \longrightarrow \text{pole}\ \Rightarrow \alpha(r)$

Example: N=5, S=½





OR 'Leading terms':

$$\begin{matrix} \alpha\beta\alpha\beta \ldots \alpha\beta & \alpha\alpha \ldots \alpha \\ N-2S & 2S \end{matrix}$$

(lowest path on branching diagram)

Find 1st β followed by α; swap that pair, return all β's to the left of that pair to their original positions.

$$\begin{matrix} \alpha\alpha\alpha \ldots \alpha & \beta\beta\beta \ldots \beta \\ \tfrac{1}{2}N+S & \tfrac{1}{2}N-S \end{matrix}$$

(final leading term)

Straightforward *correspondence* of leading terms to branching diagram paths.

Example of leading terms: N=6, S=0 $\left(f_S^N = 5\right)$

$$\alpha\beta\alpha\beta\alpha\beta$$

$$\alpha\alpha\beta\beta\alpha\beta$$

$$\alpha\beta\alpha\alpha\beta\beta$$

$$\alpha\alpha\beta\alpha\beta\beta$$

$$\alpha\alpha\alpha\beta\beta\beta$$

Pairing strategy:

- Starting from left-hand side, connect every β to the closest preceding unpaired α
- Connect any remaining α's to the pole

Examples of pairing strategy:

- $\alpha\alpha\beta\alpha\beta$

  $\Rightarrow$ singlet pairs are 2→3 and 4→5

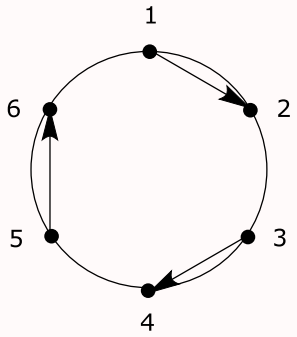
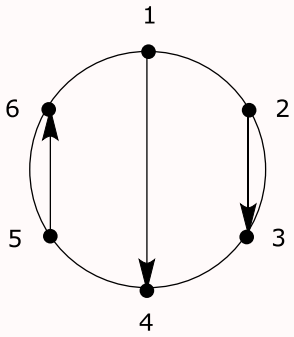
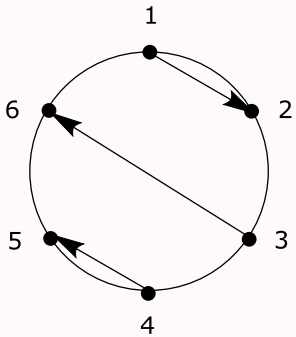
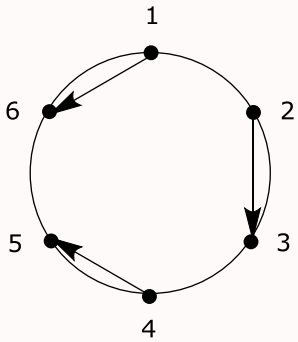
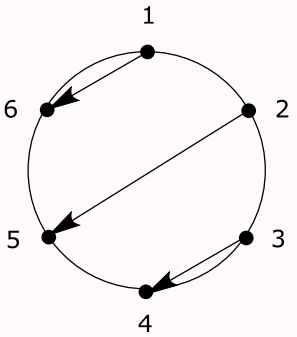
  $\Rightarrow$ (2-3,4-5,1) (k=4, N=5, S=½)

- $\alpha\alpha\alpha\beta\beta\alpha\beta\alpha\beta\beta$

  $\Rightarrow$ singlet pairs are 3→4, 2→5, 6→7, 8→9 and 1→10

  $\Rightarrow$ (1-10,2-5,3-4,6-7,8-9) (k=24, N=10, S=0)

N=6, S=0 $(f_S^N = 5)$

1	2	3	4	5
				
$\alpha\beta\alpha\beta\alpha\beta$	$\alpha\alpha\beta\beta\alpha\beta$	$\alpha\beta\alpha\alpha\beta\beta$	$\alpha\alpha\beta\alpha\beta\beta$	$\alpha\alpha\alpha\beta\beta\beta$
(1-2,3-4,5-6)	(1-4,2-3,5-6)	(1-2,3-6,4-5)	(1-6,2-3,4-5)	(1-6,2-5,3-4)

Rumer spin functions are nonorthogonal (important when calculating weights).

Order Rumer spin functions according to leading terms and then Schmidt orthogonalize

→ (standard) Kotani spin functions.

The SPINS program generates various spin functions and transforms between different bases. It also calculates weights.

"HIT ANY KEY TO CONTINUE"

http://www.liverpool.ac.uk/~dlc/dlc/SPINS.html

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% example for Aachen

 System of 4 electrons with spin 1 (f^N_S = 3)

 Renormalized input spin function coefficients (Serber spin basis):

   k   Spin-Coupling pattern   Coefficient        Weight
-------------------------------------------------------
   1:                   (10)     0.829561      0.688172
   2:                   (11)    -0.518476      0.268817
   3:                   (01)     0.207390      0.043011

 Serber to Rumer transformation

 Transformed spin function coefficients (Rumer spin basis):

   k   Spin-Coupling pattern   Coefficient     Weight    GWeight
-----------------------------------------------------------------
   1:              (1-2,3,4)    -0.159227  -0.033022   0.039436
   2:              (2-3,1,4)    -0.733236   0.648982   0.627202
   3:              (3-4,1,2)     0.462944   0.384040   0.333361
```

```
Rumer to Kotani transformation

Transformed spin function coefficients (Kotani spin basis):

  k    Spin-Coupling pattern    Coefficient         Weight
-------------------------------------------------------------
  1:           ((1/2)1(3/2))      0.377992       0.142878
  2:           ((1/2)1(1/2))     -0.902281       0.814111
  3:           ((1/2)0(1/2))      0.207390       0.043011
```

```
% example for Aachen
electrons 4 spin 1
input serber
  .8 -.5 .2
transform rumer
transform kotani
```