VALENCE BOND THEORY:

INTRODUCTION TO *AB INITIO* METHODS

David L Cooper

Department of Chemistry, University of Liverpool,

Liverpool, L69 7ZD, UK

dlc@liverpool.ac.uk
http://www.liverpool.ac.uk/~dlc

UNIVERSITY OF
LIVERPOOL

Synopsis

- Properties of the 'exact' electronic wavefunction.

- Spin eigenfunctions: Kotani; Rumer; Serber.

- General considerations: VB weights; Coulson-Fischer (& basis sets).

- Calculation of matrix elements: direct use of Löwdin formula; θÑP̂Ñ tableau functions; Moffitt method.

- Practical (?) VB approaches: VBSCF & BOVB; spin-coupled (SC), SCVB & CASVB; bioorthogonal VB.

- … and finally!

UNIVERSITY OF
LIVERPOOL

Properties of the 'Exact' Electronic Wavefunction

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

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

UNIVERSITY OF
LIVERPOOL

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

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

$$\Psi_{SM}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \sigma_1, \ldots, \sigma_N) = (f_S^N)^{-\frac{1}{2}} \sum_k^{f_S^N} \Phi_{Sk}^N(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N) \Theta_{SM;k}^N(\sigma_1, \ldots, \sigma_N)$$

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:

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

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

UNIVERSITY OF
LIVERPOOL

Paris Workshop (March 2017) [4]

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

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

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

Spin eigenfunctions $\Theta_{SM;k}^N$ <u>could</u> 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)

UNIVERSITY OF
LIVERPOOL

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

$$\Psi_{SM;k}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N; \sigma_1, \ldots, \sigma_N) = (N!)^{\frac{1}{2}} \mathcal{A}\left(\Phi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\Theta_{SM;k}^N(\sigma_1, \ldots, \sigma_N)\right)$$

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

$$\mathcal{A} = \frac{1}{N!} \sum_{P \in \mathcal{S}_N} \epsilon_P P^r P^\sigma \qquad \text{(idempotent) antisymmetrizing operator } \mathcal{A}$$

$$\Phi_{Sl}^N = \sum_k^{f_S^N} c_{Sk} \, \omega_{lk}^S \Phi$$

projection operator ω_{lk}^S

$$\omega_{lk}^S = (f_S^N / N!)^{\frac{1}{2}} \sum_{P \in \mathcal{S}_N} U_{lk}^{SN}(P) \, P^r$$

UNIVERSITY OF
LIVERPOOL

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

$$X_{kl} = \langle \Psi_{SM;k} | \hat{X} | \Psi_{SM;l} \rangle = N! \, \langle \mathcal{A}(\Phi \Theta_{SM;k}^N) | \hat{X} | \mathcal{A}(\Phi \Theta_{SM;l}^N) \rangle = \sum_{P \in \mathcal{S}_N} U_{lk}^{SN}(P) \, \langle P^r \Phi | \hat{X} | \Phi \rangle$$

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

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

☞ Second quantization …

☝ **(More) use of GL(N)?**

UNIVERSITY OF
LIVERPOOL

Spin Eigenfunctions

- Kotani

- Rumer

- Serber

"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 $\hat{S}^2$.

- 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 <u>right</u>, 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 $\mathcal{S}_{N-1}$, $\mathcal{S}_{N-2}$, ..., $\mathcal{S}_1$.

UNIVERSITY OF
LIVERPOOL

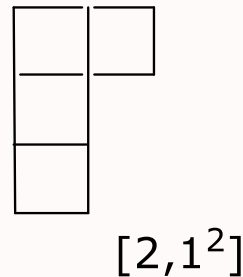$$f_S^N = f_{S+½}^{N-1} + f_{S-½}^{N-1}$$
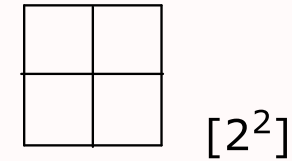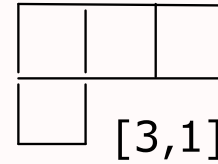
(for $S \geq ½$)

☝
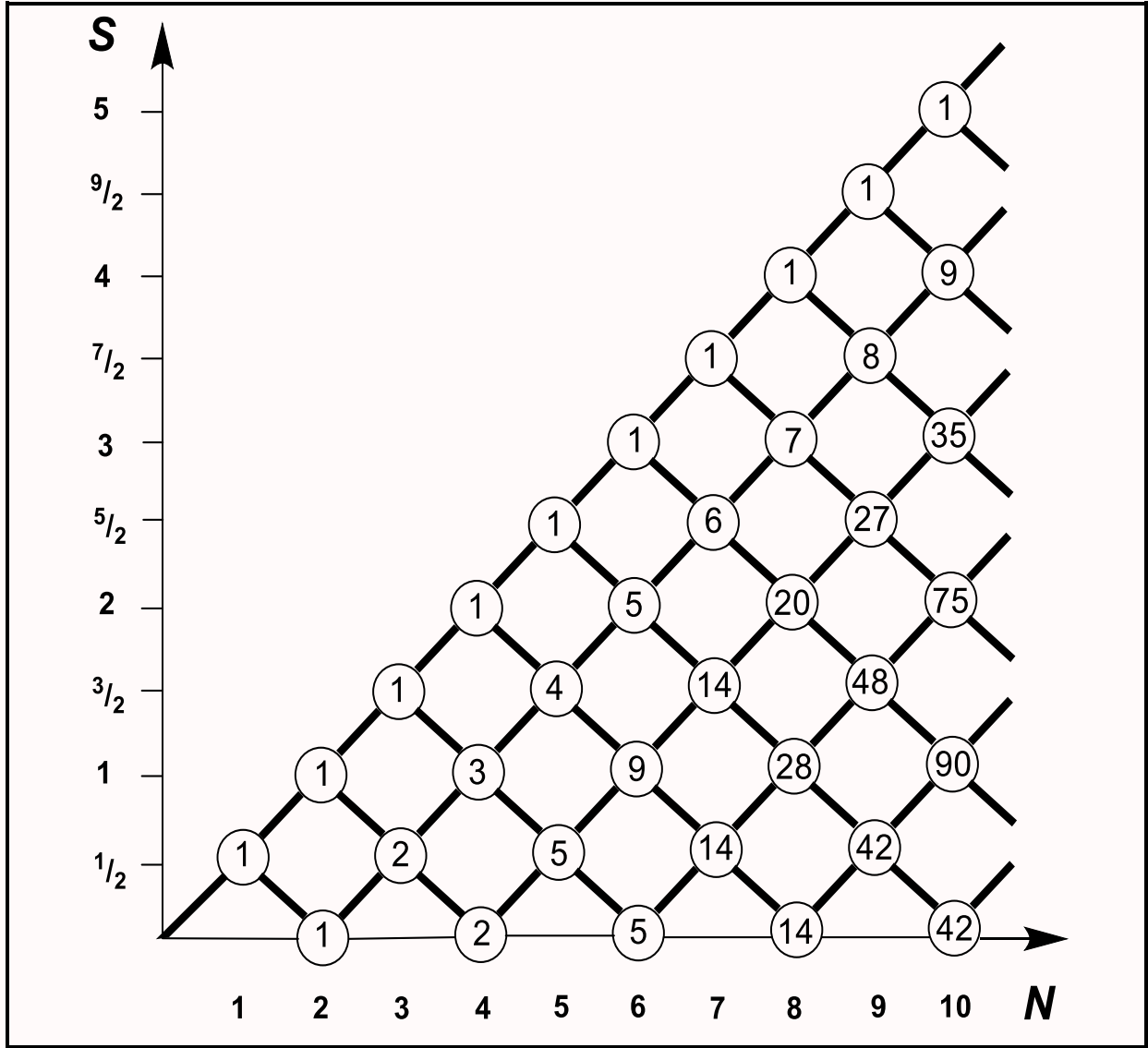
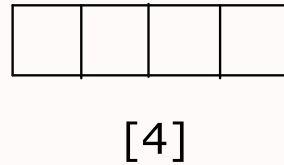f_S^N increases rather

rapidly for larger N

(extended systems?)

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

$[4]$ $[3,1]$ $[2^2]$

$[2,1^2]$ $[1^4]$
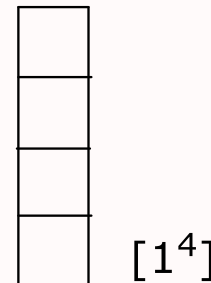
Partitions corresponding to spin functions for electrons cannot contain more than two rows (& corresponding spatial representations cannot have more than two columns).

UNIVERSITY OF LIVERPOOL

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

1	2	3
4		

$(\tfrac{1}{2}\ 1\ \tfrac{3}{2})$; $S = 1$

1	2	4
3		

$(\tfrac{1}{2}\ 1\ \tfrac{1}{2})$; $S = 1$

1	3	4
2		

$(\tfrac{1}{2}\ 0\ \tfrac{1}{2})$; $S = 1$

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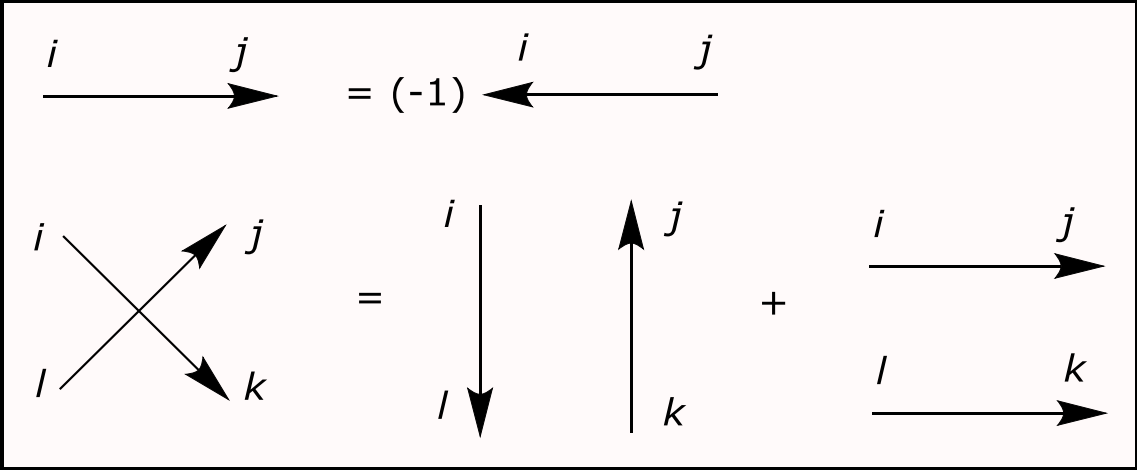
Rumer Spin Functions

- Often easy to link to bonding models – maximum pairing of electron spins.

- Basic units: singlet electron pairs (and 2S 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 2S points to the pole.

- Link the remaining $N{-}2S$ 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 $r \longrightarrow \mathrm{pole} \Rightarrow \alpha(r)$

UNIVERSITY OF
LIVERPOOL

Example: $N=5$, $S=\frac{1}{2}$
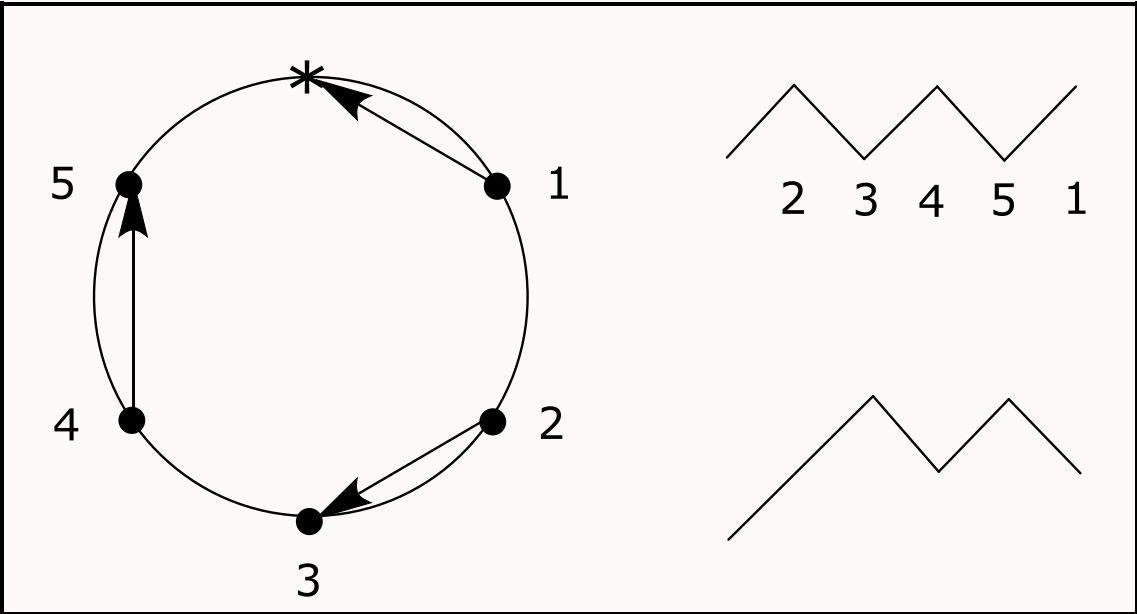
OR 'Leading terms':

$$\underset{N-2S}{\underbrace{\alpha\beta\alpha\beta\dots\alpha\beta}} \quad \underset{2S}{\underbrace{\alpha\alpha\dots\alpha}}$$

(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.

$$\underset{\frac{1}{2}N+S}{\underbrace{\alpha\alpha\alpha\dots\alpha}} \quad \underset{\frac{1}{2}N-S}{\underbrace{\beta\beta\beta\dots\beta}}$$

(final leading term)

Straightforward correspondence of leading terms to branching diagram paths.

Pairing: from left, connect every β to closest preceding α; remaining α's to the pole.

Example: $\alpha\alpha\beta\alpha\beta \Rightarrow$ singlet pairs are 2→3 and 4→5.

Rumer diagrams are nonorthogonal.

Order them according to leading terms and then Schmidt orthogonalize

$\rightarrow$ (standard) Kotani spin functions.

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).

☞ **Useful for geminal expansions?**

☝ Peter Karadakov's SPINS program generates various spin functions and transforms between different bases.

General Considerations

- VB Weights

- Coulson-Fischer (& basis sets)

Do one brave thing today... then run like hell!

VB Weights

$\Psi_{VB} = \sum_I c_I \Psi_I$	$\langle \Psi_I | \Psi_J \rangle = S_{IJ} \neq \delta_{IJ}$	weights $w(\Psi_I)$

$\sum_I w(\Psi_I) = 1$	$0 \leq w(\Psi_I) \leq 1$	$w(\Psi_I) + w(\Psi_J) = w(\Psi_I + \Psi_J)$	$\lim_{S \to I} w(\Psi_I) = |c_I|^2$
normalization	meaningful range	linearity	correct limit

- Chirgwin-Coulson ('Mulliken-like'): ☺☹☺☺ $w(\Psi_I) = \langle \Psi_{VB} | \Psi_I \rangle c_I$

- Gallup-Norbeck ('inverse-overlap'): ☺☺☹☺

$$w(\Psi_I) = \frac{x_I}{\sum_I x_I} \qquad\qquad x_I = |c_I|^2 / (\mathbf{S}^{-1})_{II}$$

(measure of 'unique component' of Ψ_I)

- Symmetric orthogonalization ('Löwdin'): ☺☺☹☺

☝ **Suggestions?**

UNIVERSITY OF
LIVERPOOL

Coulson-Fischer (H$_2$)

$$\phi_A = 1s_A + \lambda 1s_B \text{ and } \phi_B = 1s_B + \lambda 1s_A$$

$$\Psi_{CF} = [\phi_A(1)\phi_B(2) + \phi_B(2)\phi_A(1)]\Theta_{00}^2$$

- $\lambda=0$ covalent-only Heitler-London

- $\lambda=1$ basic MO

- Optimal $\lambda(R)$ corresponds to relatively small distortions of aos.

- Combines conceptual simplicity of Heitler-London model with enhanced accuracy.

- Subsumes ionic contributions into a formally covalent wavefunction – could be seen as either good or bad! (Definitions of covalent and ionic weights?)

Any given VB orbital is typically expanded **either** in full basis set **or** using basis functions associated with a given atom (or maybe atoms) $\Rightarrow$ different (a) behaviour approaching basis set limit & (b) ideas as to covalent/ionic, resonance energies, *etc*.

UNIVERSITY OF
LIVERPOOL

Calculation of Matrix Elements

- Direct use of Löwdin formula

- θÑP̂N̂ tableau functions

- Moffitt method

When you are in deep SHIT, say nothing, and try to look like you know what you're doing.

UNIVERSITY OF
LIVERPOOL

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 ($N = n_\alpha + n_\beta$):

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

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

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 $N{-}2$.

UNIVERSITY OF
LIVERPOOL

- 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.*

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

Fair range of strategies:

- Precompute low-order cofactors ($\sim n^3$). Assemble these into the required quantities (perhaps using graphical indexing).

- Cofactor-driven approach. Effort $\sim n_\alpha{}^4$ for $n_\alpha = n_\beta$

- ………

UNIVERSITY OF
LIVERPOOL

θ$\hat{N}\hat{P}\hat{N}$ Tableau Functions

Starting from an orbital product Φ we can construct a set of spatial functions Φ_{Sl} with the correct permutational symmetry through the use of an (idempotent) projection operator ω_{lk}^{S}

$$\Phi_{Sl}^{N} = \sum_{k}^{f_{S}^{N}} c_{Sk}\, \omega_{lk}^{S} \Phi \qquad\qquad E = \frac{\langle \Phi_{Sl} | \hat{H} | \Phi_{Sl} \rangle}{\langle \Phi_{Sl} | \Phi_{Sl} \rangle} \qquad \forall\ l$$

Spatial functions $\omega_{lk}^{S}\Phi$ can be chosen to carry the irrep of $\mathcal{S}_{N}$ labelled by the dual tableaux obtained by transposing the Young frames. Inserting orbital indices → Weyl tableaux.

Gallup's $\theta\hat{N}\hat{P}\hat{N}$ approach corresponds to a particular choice of ω_{lk}^{S} and to associating Φ_{Sl}

with the Weyl tableau:
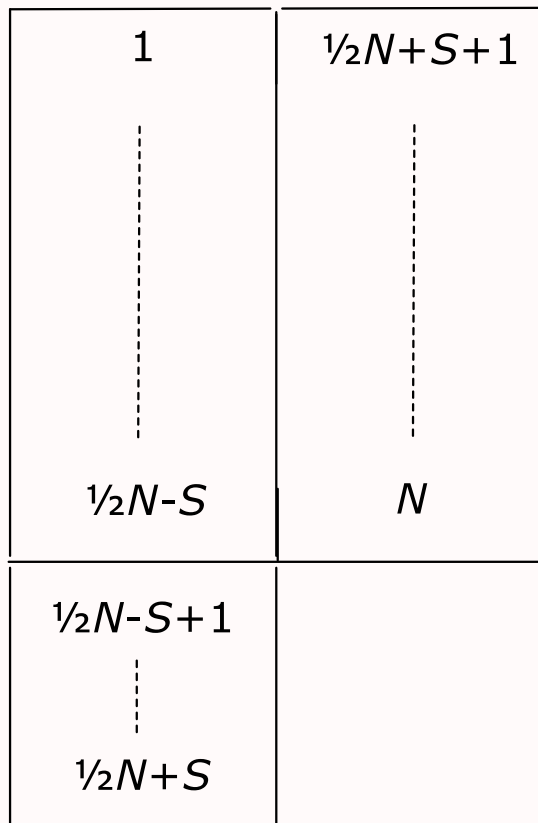
$\frac{1}{2}N-S$

$2S$

"highest path on

Branching diagram"

Remaining $(f_{S}^{N}-1)$ members

of set can be obtained by

permuting orbital indices.

$\omega_{11}^S = \theta\widehat{N}\widehat{P}\widehat{N}$ [$\widehat{N}$ (<u>n</u>egative) is product of antisymmetrizers on columns; $\widehat{P}$ (<u>p</u>ositive) is symmetrizer on rows]

θ is chosen so that coefficient of the identity is $f_S^N/N!$

$N \times N$ masking matrix (all values are 1 except where shown):

$$\boldsymbol{w}(q) = \left. \left(\begin{array}{c|c|c|c} & & \mathbf{0} & \\ \hline \mathbf{0} & & & \begin{matrix} q & \cdots & q \\ q & \cdots & q \end{matrix} \end{array} \right) \begin{array}{l} \tfrac{1}{2}N + S \\[2.5em] \tfrac{1}{2}N - S \end{array} \right.$$

$$\quad\quad p \quad\quad \tfrac{1}{2}N + S - p \quad\quad p \quad\quad \tfrac{1}{2}N - S - p$$

Defining 'masked orbital determinants' $\Delta_\Phi(q)$ such that (i,j) element is $w_{ij}(q)u_j(i)$ can rewrite a tableau function Ψ as a sum of $\sim\frac{1}{2}(\frac{1}{2}N-S+2)$ terms (often no more than 3):

$$\Psi = K_{NpS} \sum_k C_k \, \Delta_\Phi(q_k)$$

$$K_{NpS} = \frac{f_S^N}{N!} \frac{\frac{1}{2}N + S + 1}{\frac{1}{2}N + S - p + 1}$$

Values of $C_k(N-2p,S)$ and $q_k(N-2p,S)$ are tabulated (at least to N=10 and $S=\frac{5}{2}$)

Define modified determinant of orbital overlaps $D_{UV}^{(q)}$ such that (i,j) element is $w_{ij}(q)\langle u_i|v_j\rangle$

Required matrix elements essentially obtained from application of Löwdin formula (using cofactors of $D_{UV}^{(q)}$)

UNIVERSITY OF LIVERPOOL

Example:

$$\left\langle \Psi_U \left| \frac{1}{r_{12}} \right| \Psi_V \right\rangle = K_{NpS} \sum_k \left[C_k \sum_{i,j,l,m}^N \left\langle u_i u_j \left| \frac{1}{r_{12}} \right| v_l v_m \right\rangle w_{il}(q_k) w_{jm}(q_k) \left[D_{UV}^{(q_k)}(ij|lm) \right] \right]$$

$$D_{UV}^{(q_k)}(ij|lm) = \frac{D_{UV}^{(q_k)}(i|l) D_{UV}^{(q_k)}(j|m) - D_{UV}^{(q_k)}(i|m) D_{UV}^{(q_k)}(j|l)}{D_{UV}^{(q_k)}}$$

Drawbacks? Orbital-based (no α/β spin factorization); full spin space

☞ **Worth revisiting?**

UNIVERSITY OF LIVERPOOL

Moffitt Method (Orthogonalization)

Slater determinants $\{U\}$ built from nonothogonal spin-orbitals $\{u\}$

Basic recipe:

- Order $\{u\}$: α before β; more often occupied u_i before less often occupied

- Schmidt orthogonalize → orthogonal orbitals $\{\varphi\}$ (& Slater determinants $\{\Phi\}$)

- Using determinants $\{\Phi\}$, calculate matrix elements (Slater-Condon rules);

  N.B. need two-electron integrals in the orthogonalized orbitals basis

- Use transformation matrix between $\{U\}$ and $\{\Phi\}$ to back-transform matrix

  elements to the nonorthogonal basis.

Practical (?) VB Approaches

- VBSCF

- Breathing Orbital VB (BOVB)

- Spin-coupled (SC), SCVB & CASVB

- Bioorthogonal VB (*another* BOVB)

"HIT ANY KEY TO CONTINUE"

UNIVERSITY OF
LIVERPOOL

VBSCF

Generalized Brillouin theorem: $$\langle \Psi_0 | \hat{H} - E_0 | \Psi_{ij} \rangle = 0$$	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 1$^{\text{st}}$ 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 $$\Psi_{\text{BI}} = b_0 \Psi_0 + \sum_{ij} b_{ij} \Psi_{ij}$$	summation over all linearly independent excitations that can change the energy

UNIVERSITY OF
LIVERPOOL

Basic recipe:

- Choose starting orbitals and list of VB structures.

- Solve secular equations $\rightarrow$ first Ψ_0

- Minimize energy of $\Psi_{\mathrm{BI}} \rightarrow$ updated orbitals $\rightarrow$ new Ψ_0

- Iterate until $b_0 \approx 1$ and all $b_{ij} \approx 0$

VBCI: larger VB built from the optimized VBSCF orbitals

Also VBPT2, VB-QMC ...

Observations:

- Relatively cheap iterations, but can be many of them. Test that stationary point is actually a (local) minimum?

- In newer programs, 1st-order scheme is replaced by 2nd-order (Newton-Raphson-like) nearer convergence. (Also: identify that stationary point is actually a (local) minimum.)

- XMVB is a particularly efficient code for VBSCF (and beyond)

Breathing Orbital VB (BOVB)

- Typically use so-called **strictly localized orbitals** for active/valence electrons, with either localized (L) or delocalized (D) spectator orbitals.

- Instead of a common set of nonorthogonal orbitals (as in simplest form of VBSCF) use different orbitals for different VB structures. E.g. optimal orbitals for covalent $X-Y$ and for ionic (X^-Y^+, X^+Y^-) structures will differ. [Basis sets!]

- The two X^- active electrons in X^-Y^+ could occupy a doubly-occupied orbital or, better, two different orbitals. This split (S) $\Rightarrow$ radial correlation. (Similarly Y^-.)

- Various levels of breathing orbital VB (L or D; S or not): L-BOVB, SD-BOVB *etc.*

- BOVB approaches aim to take account of aspects of dynamic correlation that vary during a process.

UNIVERSITY OF LIVERPOOL

Spin-coupled (SC), SCVB & CASVB

Exact solution:

$$\Psi_{SM}(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N;\sigma_1,\dots,\sigma_N) = \sum_k^{f_S^N} c_{Sk}\,(N!)^{\frac{1}{2}}\,\mathcal{A}\left(\Phi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N)\Theta_{SM;k}^N(\sigma_1,\dots,\sigma_N)\right)$$

Active space of *basic* spin-coupled (SC) or full-GVB wavefunction:

$$\Phi(\boldsymbol{r}_1,\dots,\boldsymbol{r}_N) = \varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2)\dots\varphi_N(\boldsymbol{r}_N)$$

Usually expand orbitals in full basis set (i.e. no 'strict localization' conditions) and active-space spin function in complete spin space.

Newton-Raphson-like schemes: $(\mathbf{G} + \alpha\mathbf{I})\delta\boldsymbol{c} = -\mathbf{g}$

UNIVERSITY OF LIVERPOOL

At convergence can obtain 'stacks' of virtual orbitals (essentially determined in field of $N-1$ electrons) → can perform nonorthogonal CI ("SCVB") to account for dynamical correlation (& higher roots describe excited states.)

Resulting SCVB expansions are still compact and easy to interpret. Often dominated by SC configuration (or simple excitations from it).

Generalizations of *basic* SC or full-GVB include SC(N,M), GMCSC, …

Strategies for SC:

- $\mathcal{S}_N$:

$$D(\mu_1\mu_2\ldots\mu_N|\nu_1\nu_2\ldots\nu_N) = \sum_{k,l}^{f_S^N} c_{Sk}c_{Sl}\{U_{kl}^{SN}(\mathrm{P}) \oplus U_{lk}^{SN}(\mathrm{P})\} \qquad \mathrm{P} = \begin{pmatrix} \mu_1\mu_2\ldots\mu_N \\ \nu_1\nu_2\ldots\nu_N \end{pmatrix}$$

$$D(\mu_1\mu_2\ldots\mu_{N-1}|\nu_1\nu_2\ldots\nu_{N-1}) = \sum_{\nu_N} D(\mu_1\mu_2\ldots\mu_{N-1}\mu_N|\nu_1\nu_2\ldots\nu_{N-1}\nu_N)\langle\mu_N|\nu_N\rangle$$

$\rightarrow\rightarrow\rightarrow$ density matrices of order 4, 3, 2, …

- Expand in determinants → cofactors …

- Variationally 'project' from CASSCF (using CASVB algorithms)

CASVB algorithms (Basic Idea)

Full CI wavefunctions are invariant to nonsingular transformations of defining orbitals:

$$\Psi_{\text{CAS}} = \sum_I^{N_{\text{CI}}} c_I \Psi_I$$

(normalized)

$\{\phi'\} = \{\phi\}\, \mathbf{O} \quad \Rightarrow \quad \{\Psi'\} = \{\Psi\}\, \mathbf{T}(\mathbf{O})$

m orbitals $\qquad N_{\text{CI}}$ structures

$\mathbf{O} = \mathbf{O}_1 \mathbf{O}_2 \quad \Leftrightarrow \quad \mathbf{T}(\mathbf{O}) = \mathbf{T}(\mathbf{O}_1)\mathbf{T}(\mathbf{O}_2)$

$$\left(\mathbf{O}_{11}(\lambda_1)\mathbf{O}_{12}(\lambda_2)\mathbf{O}_{13}(\lambda_3)\dots\mathbf{O}_{mm}(\lambda_{m^2})\right)^{-1}\mathbf{O} = \mathbf{I}$$

$\mathbf{O}_{ij}(\lambda): \phi_j \rightarrow \phi_j + \lambda\phi_i$

$\mathbf{T}\left(\mathbf{O}_{ij}(\lambda)\right)$ is fairly simple

Generate (exactly) effects of $\mathbf{T}(\mathbf{O})$ (without explicit construction); also convenient expressions for first and second derivatives of $\mathbf{T}(\mathbf{O})$ with respect to the λ parameters.

UNIVERSITY OF
LIVERPOOL

CASVB algorithms (Optimization Criteria – Choice of 0)

Seek Ψ_{VB} which dominates $\Psi_{CAS} = S_{VB}\Psi_{VB} + \left(1 - S_{VB}{}^2\right)^{\frac{1}{2}}\Psi_{VB}^{\perp}$

maximize $S_{VB} = \dfrac{\langle\Psi_{CAS}|\Psi_{VB}\rangle}{\langle\Psi_{VB}|\Psi_{VB}\rangle^{\frac{1}{2}}}$ overlap criterion (relatively inexpensive)	$E_{VB} = \dfrac{\langle\Psi_{VB}|\hat{H}|\Psi_{VB}\rangle}{\langle\Psi_{VB}|\Psi_{VB}\rangle}$ energy criterion (more expensive)

- Obtain *exact* representations of 'N in m' CASSCF wavefunctions in which a small number of VB structures dominate.
- Analogous overlap- and energy-optimized wavefunctions typically in good qualitative agreement.

BUT: Risks in overlap-based "VB readings" of MO wavefunctions if we do not keep ALL structures? High overlap need not mean energetically any good!

UNIVERSITY OF
LIVERPOOL

CASVB algorithms (fully-variational calculations)

Embed CASVB algorithms in CASSCF (MOLPRO/MOLCAS)

Alternate CASVB E_{VB} optimization (nonorthogonal) with CASSCF core-active, core-virtual and active-virtual orbital rotations (orthogonal)

→ fully-variational wavefunctions such as (MC)SC

☞ SC(N,M)

Bioorthogonal VB (*another* BOVB)

$\langle \phi_\mu | \phi_\nu \rangle = s_{\mu\nu}$	$\langle \tilde{\phi}_\mu | \phi_\nu \rangle = \delta_{\mu\nu}$	$\{\tilde{\phi}\} = \{\phi\}\mathbf{s}^{-1}$
$\tilde{E} = \dfrac{\langle \widetilde{\Psi}(\tilde{\mathbf{x}}) | \hat{H} | \Psi(\mathbf{x}) \rangle}{\langle \widetilde{\Psi}(\tilde{\mathbf{x}}) | \Psi(\mathbf{x}) \rangle}$	$\dfrac{\partial}{\partial \tilde{x}_i} \dfrac{\langle \widetilde{\Psi}(\tilde{\mathbf{x}}) | \hat{H} | \Psi(\mathbf{x}) \rangle}{\langle \widetilde{\Psi}(\tilde{\mathbf{x}}) | \Psi(\mathbf{x}) \rangle} = 0 \quad \forall\, i$ (optimal $\Psi(\mathbf{x})$)	$\dfrac{\partial}{\partial x_i} \tilde{E} \neq 0$ (in general)

- Not a symmetrical variational problem (H and S are not symmetric).

- Obtain right-hand eigenvectors. [Can be formulated as matrix diagonalization.]

- $|E - \tilde{E}|$ mostly linked to (lower) quality of dual wavefunction

- Could in principle be used with larger N – but what about f_s^N?

☝ **Worth revisiting?**

... and Finally (Lest we Forget)!

👉 Why do we even bother with VB (*et al*)?

"Physically and ideologically inadmissible notions formulated by decadent bourgeois scientists"

I have no idea what you're talking about...
...so here's a bunny with a pancake on its head.