The calculation of matrix elements

$$\Phi = \sum s_d \Delta_d$$

A structure or Brillouin state is a lineair combination of determinants

$$\langle \Phi_A | H | \Phi_B \rangle = \sum_{de} s_{dA} s_{eB} \langle \Delta_d | H | \Delta_e \rangle$$

The matrix elements are linear combinations of matrix elements over determinants

One may apply group theory (McWeeny, Wu,Li et al.)

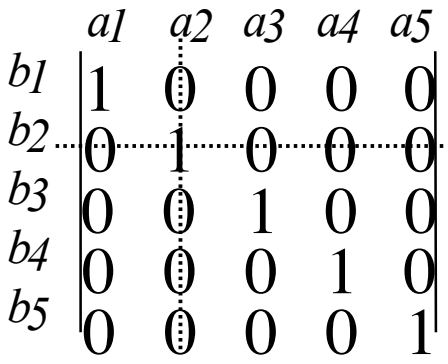
Slater Rules

(1-electron)

$$\sum_{i}^{N} \langle A|h(i)|B\rangle$$

WORK

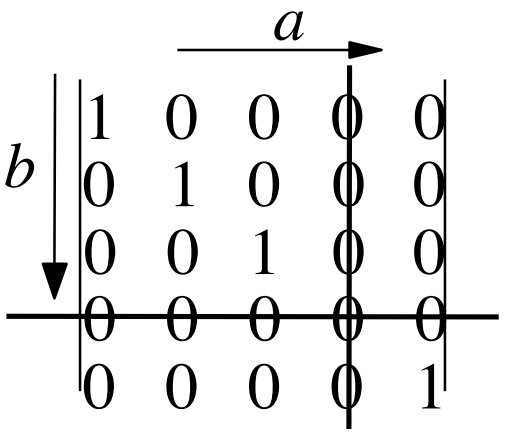
$S_{A=B}$



N

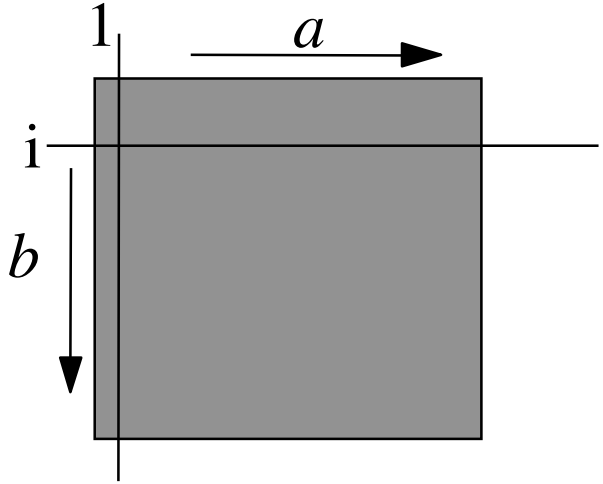
$S_{A\neq B}$

a4≠b4



1

$S_{A\neq B}$



N^3

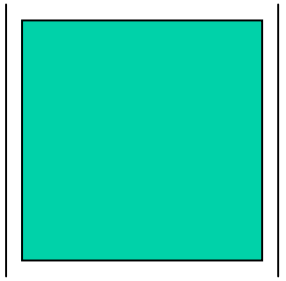
Determinants

$$|A| = \begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix} = A_{11} * A_{22} - A_{12} * A_{21}$$

$$|B| = \sum_{P}^{N!} (-1)^{p} P(abcd..) B_{1a} B_{2b} B_{3c} \ldots B_{Nz}$$

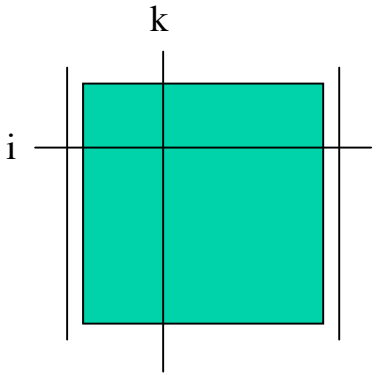
- A Determinant is not changed when
  - the matrix is transposed
  - a row/column multiplied by a constant is added to another
- A Determinant is linear in it's elements
- When row/columns are interchanged => sign := sign***-1**
- |ABC| = |A|.|B|.|C|
- The order of the determinant is the dimension of the matrix
- Nullity of matrix: dimension-rank (= # independent rows/columns

Determinant

$|B|=$ 

$$|A| = \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix}$$

Cofactor

$B^{(i,k)}=-1^{i+k}$ 

$$A^{(3,2)} = -\begin{vmatrix} a_{11} & a_{13} & a_{14} \\ a_{21} & a_{23} & a_{24} \\ a_{41} & a_{43} & a_{44} \end{vmatrix}$$

Cofactor weight of matrix-element in determinant

Matrix Element - 1-electron-simple

$$\mathrm{A} = (a_1 a_2 a_3) \qquad \mathrm{B} = (b_1 b_2 b_3)$$

$$\langle A|H_1|B\rangle = \sum_i^3 \langle A|h(i)|B\rangle \quad H_1 = h(1)+h(2)+h(3)$$

$$\langle A|h(1)|B\rangle = \langle a_1 a_2 a_3|h(1)|b_1 b_2 b_3\rangle =$$

$$= \langle a_1|h(1)|b_1\rangle\langle a_2|b_2\rangle\langle a_3|b_3\rangle = h_{a_1 b_1} s_{a_2 b_2} s_{a_3 b_3}$$

$$\langle A|H_1|B\rangle = h_{a_1 b_1} s_{a_2 b_2} s_{a_3 b_4} + s_{a_1 b_1} h_{a_2 b_2} s_{a_3 b_4} + s_{a_1 b_1} s_{a_2 b_2} h_{a_3 b_4}$$

$$\langle A|B\rangle = s_{a_1 b_1} s_{a_2 b_2} s_{a_3 b_4}$$

Suppose only $s_{a_1 b_1} = 0$

$$\langle A|H_1|B\rangle = h_{a_1 b_1} \underbrace{s_{a_2 b_2} s_{a_3 b_3}}_{\textit{Cofactor}}$$

Cofactors/minors,compounds adjugates

A minor (order n) is the determinant of a n by n submatrix, constructed from the original matrix by removing (N-n) rows and colums.
A cofactor (order N-n)is a signed minor.

$$k^{th} \text{ order cofactor } : B^{(i_1,i_2,\ldots,i_k,j_1,j_2,\ldots,j_k)}$$

$$\text{sign} : \left(-1\right)^{\sum_{m}^{N-n} i_m + j_m}$$

The k^{th} order compound matrix ($A^{(k)}$) is the matrix with k^{th} order minors.
The indexing is from rows/columns of minor-matrix.

second order compound matrix

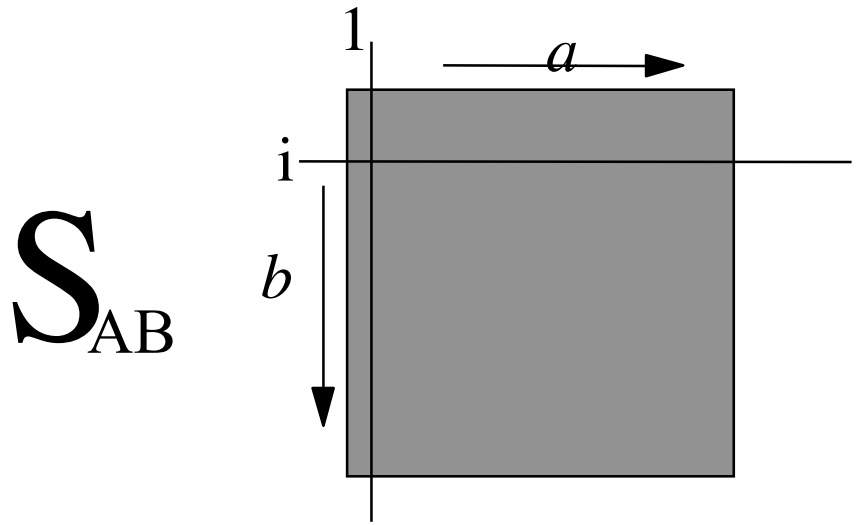
$$(A)^{(2)}_{ij,kl} = \begin{vmatrix} A_{ik} & A_{jk} \\ A_{il} & A_{jl} \end{vmatrix}$$

The k^{th} order adjugate ($adj^{(k)}(B)$) is the matrix with k^{th} order cofactors. The indexing is by removed rows/columns - transposed.
So the first order cofactor $B^{(1,2)}$ is at position (2,1).

Matrix Element

$$\mathbf{A} = |a_1 a_2 a_3 \ldots\ldots a_n| \qquad B = |b_1 b_2 b_3 \ldots\ldots b_n|$$

$$\langle A|H|B\rangle = \sum_i^n \langle A|h(i)|B\rangle + \sum_{i<j}^N \langle A|\tfrac{1}{r_{ij}}|B\rangle$$



$$\langle h(1)_{AB}\rangle = \sum_i^n \langle a_1(1)|h(1)|b_i(1)\rangle . S_{AB}^{(1,i)}$$

$$\langle A|H|B\rangle = Tr[h_{AB}.adj(S_{AB})] + Tr[G_{AB}.adj^{(2)}(S_{AB})]$$

Lowdin

Rules for adjugates and compound matrices

$$B^{(k)}\left(adj^{(k)}(B)\right) = \left(adj^{(k)}(B)\right)B^{(k)} = |B| I$$

For k = 1:

$$adj(B) = |B| B^{-1}$$

$$adj^{(k)}(ABC) = adj^{(k)}(C)\, adj^{(k)}(B)\, adj^{(k)}(A)$$

$$\left(B^{(k)}\right)^{-1} = \left(B^{-1}\right)^{(k)}$$

Jacobi ratio theorem

$$\left(adj(B)\right)^{(k)} = |B|^{k-1} adj^{(k)}(B)$$

See A.C. Aitken,
Determinants and Matrices
McGraw-Hill, New York (1968)

The energy of a Valence Bond Wave function

$$\Psi = \sum_p C_p \Delta_p$$

$$\left\langle \Delta_p \middle| \hat{H} \middle| \Delta_q \right\rangle = \sum_{ik} h_{ik} \mathbf{S}^{(i,k)} + \sum_{i<j,k<l} \left\{ \langle ij|kl\rangle - \langle ij|lk\rangle \right\} \mathbf{S}^{(i,j,k,l)}$$ Löwdin

$$\left\langle \Delta_p \middle| \Delta_q \right\rangle = |\mathbf{S}| = \sum_i S_{ik} S^{(i,k)}$$ Expand determinant along a column

$$E = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \sum_p \sum_q C_p C_q \left(\sum_{ik} h_{ik} \mathbf{S}_{pq}^{(i,k)} + \sum_{i<j,k<l} \left\{ \langle ij|kl\rangle - \langle ij|lk\rangle \right\} \mathbf{S}_{pq}^{(i,j,k,l)} \right)$$

Cofactors are 0.0 if no i,j,k,l

$$E = \langle \Psi | H | \Psi \rangle = \left(\sum_{ik} h_{ik} d_{ik} + \sum_{i<j,k<l} \left\{ \langle ij|kl\rangle - \langle ij|lk\rangle \right\} D_{ijkl} \right)$$

same expression as usual

$$d_{ik} = \sum_p \sum_q \mathbf{S}_{pq}^{(i,k)} C_p C_q$$

$$D_{ijkl} = \sum_p \sum_q \mathbf{S}_{pq}^{(i,j,k,l)} C_p C_q$$

Hellmann-Feynman Theorem

$$\frac{dE}{dx} = \left\langle \Psi \left| \frac{\partial \hat{H}}{\partial x} \right| \Psi \right\rangle$$ For exact wave functions

$$\frac{dE(x)}{dx} = \frac{\delta E(x:c)}{\delta x} + \cancel{\frac{\delta E(x:c)}{\delta c}}\ \cancel{\frac{\delta c}{\delta x}} = \frac{\delta E(x:c)}{\delta x}$$

C is either optimised or fixed

- Orbitals
- Structure coefficients

- Orbital coefficients
- Exponents

Thus the gradient (e.g. with respect to nuclear coordinates) may be evaluated as the expectation value of the Hamiltonian. This would only involve 1-electron integrals if the basis-functions weren't geometry dependent.

Valence Bond Gradients

Ψ normalised : $L = E - \lambda[S-1] = \langle \Psi | \hat{H} | \Psi \rangle - \lambda[\langle \Psi | \Psi \rangle - 1]$

What is λ ?

$$\frac{\partial L}{\partial C_k} = \frac{\partial}{\partial C_k}\left\{\sum_{ij} C_i C_j H_{ij} - \lambda\left[\sum_{ij} C_i C_j S_{ij} - 1\right]\right\} = 2\sum_i C_i\{H_{ik} - \lambda S_{ik}\} = 0$$

$$\sum_i C_i\{H_{ik} - ES_{ik}\} = 0$$

} λ=E

so $\boxed{\frac{\partial E}{\partial x} = \frac{\partial L}{\partial x} = \frac{\partial}{\partial x}\langle \Psi | \hat{H} | \Psi \rangle - E\frac{\partial}{\partial x}\langle \Psi | \Psi \rangle}$ or differentiate $\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$

$$\frac{\partial E}{\partial x} = \left(\sum_{ik} \frac{\partial h_{ik}}{\partial x}.d_{ik} + \sum_{i<j,k<l}\left\{\frac{\partial \langle ij|kl\rangle}{\partial x} - \frac{\partial \langle ij|lk\rangle}{\partial x}\right\}D_{ijkl}\right)$$

$$+\left(\sum_{ik} h_{ik}\frac{\partial d_{ik}}{\partial x} + \sum_{i<j,k<l}\{\langle ij|kl\rangle - \langle ij|lk\rangle\}\frac{\partial}{\partial x}D_{ijkl}\right) - E\frac{\partial \langle \Psi|\Psi\rangle}{\partial x}$$

Derivatives of Cofactors

Derivatives of Cofactors/Density Matrices

$$|\mathbf{S}| = \sum_{i}^{N} s_{ik} S^{(i,k)}$$

$$\frac{d|\mathbf{S}|}{dx} = \sum_{i}^{N} \left[\frac{ds_{i1}}{dx} S^{(i,1)} + s_{i1} \frac{dS^{(i,1)}}{dx} \right]$$

$$= \sum_{i}^{N} \left[\frac{ds_{i1}}{dx} S^{(i,1)} + \frac{ds_{i2}}{dx} S^{(i,2)} + ... \right] = \sum_{rs} \frac{ds_{rs}}{dx} \mathbf{S}^{(r,s)}$$

$$\frac{d\mathbf{S}^{(i,k)}}{dx} = (sign) \sum_{rs} \frac{dS_{rs}}{dx} \mathbf{S}^{(i,r,k,s)}$$

$$\frac{d\mathbf{S}^{(i,j,k,l)}}{dx} = (sign) \sum_{rs} \frac{dS_{pq}}{dx} \mathbf{S}^{(i,j,r,k,l,s)}$$

$$\frac{\partial \langle \Psi | \Psi \rangle}{\partial x} = \sum_{p} \sum_{q} C_p C_q \frac{d|\mathbf{S}_{pq}|}{dx} = \sum_{rs} \frac{ds_{rs}}{dx} \sum_{p} \sum_{q} C_p C_q \mathbf{S}_{pq}^{(r,s)} = \sum_{rs} \frac{ds_{rs}}{dx} d_{rs}$$

$$\frac{\partial d_{ik}}{\partial x} = \sum_{rs} \frac{ds_{rs}}{dx} \sum_{p} \sum_{q} \mathbf{S}_{pq}^{(i,r,k,s)} C_p C_q = \sum_{rs} \frac{ds_{rs}}{dx} d_{irks}$$

$$\frac{\partial D_{ijkl}}{\partial x} = \sum_{rs} \frac{ds_{rs}}{dx} \sum_{p} \sum_{q} \mathbf{S}^{(i,j,r,k,l,s)} C_p C_q = \sum_{rs} \frac{ds_{rs}}{dx} d_{ijrkls}$$

Derivative of a determinant ('simple')

$$|\mathbf{S}| = \begin{vmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{vmatrix} = s_{11}\begin{vmatrix} s_{22} & s_{23} \\ s_{32} & s_{33} \end{vmatrix} - s_{21}\begin{vmatrix} s_{12} & s_{13} \\ s_{32} & s_{33} \end{vmatrix} + s_{31}\begin{vmatrix} s_{12} & s_{13} \\ s_{22} & s_{23} \end{vmatrix}$$

$$= s_{11}\left(s_{22}s_{33} - s_{32}s_{23}\right) - s_{21}\left(s_{12}s_{33} - s_{32}s_{13}\right) + s_{31}\left(s_{12}s_{23} - s_{22}s_{13}\right)$$

$$\frac{d|\mathbf{S}|}{dx} = \left(s_{22}s_{33} - s_{32}s_{23}\right)\frac{ds_{11}}{dx} + s_{11}\frac{d\left(s_{22}s_{33} - s_{32}s_{23}\right)}{dx} + \cdots\cdots$$

$$= S^{(1,1)}\frac{ds_{11}}{dx} + s_{11}\frac{dS^{(1,1)}}{dx} + \cdots\cdots$$

$$\frac{dS^{(1,1)}}{dx} = s_{33}\frac{ds_{22}}{dx} + s_{22}\frac{ds_{33}}{dx} - s_{32}\frac{ds_{23}}{dx} - s_{23}\frac{ds_{32}}{dx} = s_{33}\frac{dS^{(1,1,33)}}{dx} + \cdots\cdots$$

$$\frac{d|\mathbf{S}|}{dx} = s_{22}s_{33}\frac{ds_{11}}{dx} + s_{11}s_{33}\frac{ds_{22}}{dx} + s_{11}s_{22}\frac{ds_{33}}{dx} + \cdots\cdots = \sum_{rs}\frac{ds_{rs}}{dx}\mathbf{S}^{(r,s)}$$

More determinants : $$d_{ik} = \sum_{p}\sum_{q} S_{pq}^{(i,k)} C_p C_q$$

Derivative Expression

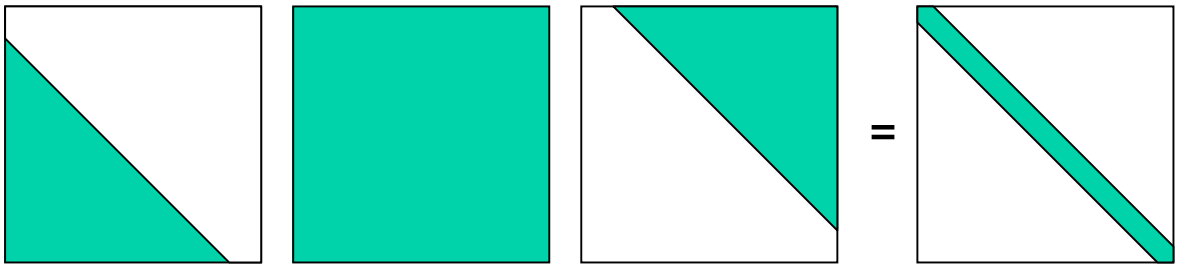
Gradient integrals

$$\frac{\partial E}{\partial x} = \left(\sum_{ik} \frac{\partial h_{ik}}{\partial x} . d_{ik} + \sum_{i<j,k<l} \left\{ \frac{\partial \langle ij | kl \rangle}{\partial x} - \frac{\partial \langle ij | lk \rangle}{\partial x} \right\} D_{ijkl} \right) - \sum_{ik} \frac{\partial s_{ik}}{\partial x} . L_{ik}$$

$$L_{ik} = E_0 . d_{ik} - \sum_{rs} h_{rs} d_{risk} - \sum_{r<j,s<l} \{ \langle rj | sl \rangle - \langle rj | ls \rangle \} D_{rjislk}$$

Lagrangian generated in TURTLE
Used in the normal place in a MCSCF-gradient code

Cofactors



- *Asymmetric Schmidt / biorthogonalisation (non-unitary)*
- *Asymmetric Löwdin / singular value decomposition / corresponding orbital transformation*

$$\mathbf{d} = \mathbf{L}\cdot\mathbf{S}\cdot\mathbf{R}$$
$$|\mathbf{L}| = |\mathbf{R}| = 1$$
$$\mathbf{S} = \mathbf{L}^{-1}\cdot\mathbf{d}\cdot\mathbf{R}^{-1}$$

$$|\mathbf{S}| = |\mathbf{d}| = \prod_{i=1}^{N} d_{ii}$$

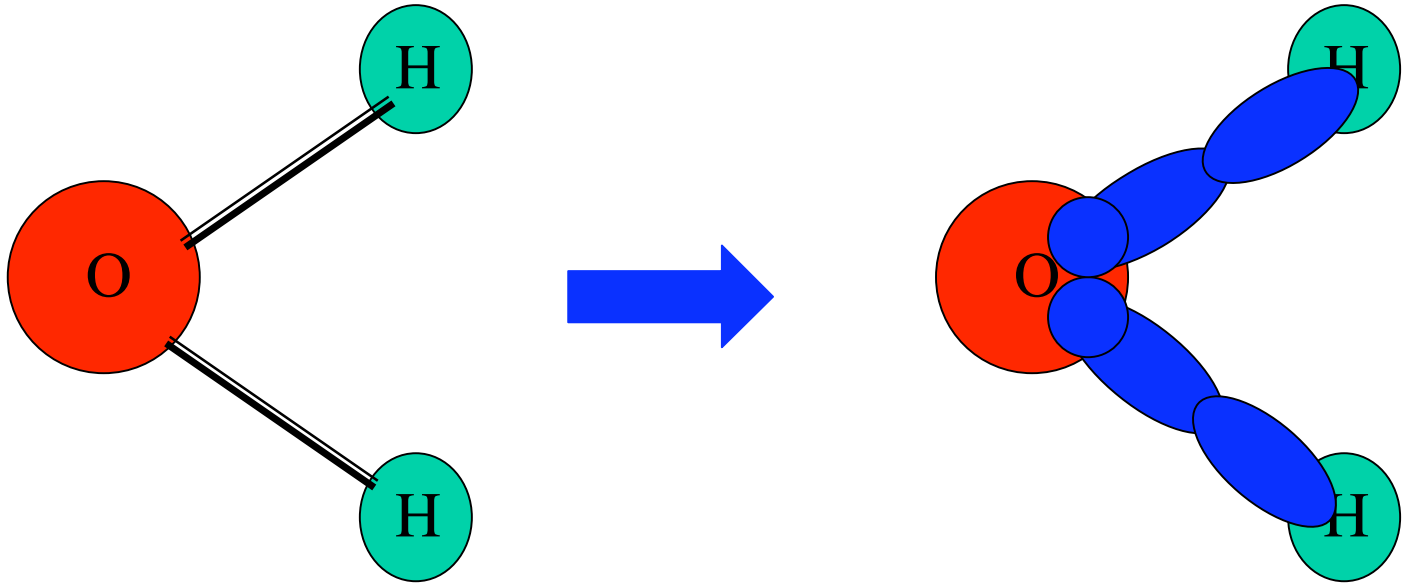
$$O\left(N^3\right) operations$$

$$adj(\mathbf{S}) = adj(\mathbf{L}^{-1}\cdot\mathbf{d}\cdot\mathbf{R}^{-1}) = adj(\mathbf{R}^{-1})\cdot adj(\mathbf{d})\cdot adj(\mathbf{L}^{-1}) = \mathbf{R}\cdot adj(\mathbf{d})\cdot\mathbf{L}$$

$$|S|S^{-1}$$

$$|d|d^{-1}$$

Application of singular value decomposition



Per bond (automatically detected (?)) generate overlap matrix between orbitals of the atoms. Then do a singular value decomposition which generates the transformation to orbitals that maximise the overlap.

See also
O. Alter, P. O. Brown and D. Botstein
"*Singular value decomposition for genome-wide expression data processing and modeling*"
Proceedings of the National Academy of Sciences 97 (18), pp. 10101–10106 (August 2000).

Nullity : # zero's in **d**

Nullity 0

$$adj(d) = |d|.d^{-1}$$

$$\mathbf{adj(S) = R.adj(d)L}$$

$$\mathbf{adj^{(k)}(S) = |S|^{1-k}\left(adj(S)\right)^{(k)}}$$

second order compound matrix

$$(A)^{(2)}_{ij,kl} = \begin{vmatrix} A_{ik} & A_{jk} \\ A_{il} & A_{jl} \end{vmatrix}$$

(Jacobi ratio theorem)

Nullity 1

$$\mathbf{d} = \begin{pmatrix} x & 0 & 0 & 0 \\ 0 & x & 0 & 0 \\ 0 & 0 & x & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad \mathbf{adj(d)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & x \end{pmatrix}$$

$$\mathbf{adj(S) = R.adj(d)L}$$

Nullity 1

Change element of S

$$S'_{pq} = S_{pq} + t$$

$$|\mathbf{S}'(t)| = |\mathbf{S}| + t\mathbf{S}^{(p,q)}$$

$$\mathbf{S}'(t)^{(i,l)} = \mathbf{S}^{(i,l)} + (sign)t\mathbf{S}^{(i,p,l,q)}$$

$$\mathbf{S}'(t)^{(i,j,l,m)} = \mathbf{S}^{(i,j,l,m)} + (sign)t\mathbf{S}^{(i,j,p,l,m,q)}$$

$$\mathbf{S}'(t)^{(i,j,k,l,m,n)} = \mathbf{S}^{(i,j,k,l,m,n)} + (sign)t\mathbf{S}^{(i,j,k,p,l,m,n,q)}$$

…

Determinants linear, interpolate (t=+1,t=-1)

$$adj^{(n)}(\mathbf{S}) = \frac{1}{2}\left(adj^{(n)}(\mathbf{S}'(1)) + adj^{(n)}(\mathbf{S}'(-1))\right)$$

Nullity 2

First order cofactors :0

Interpolate using 2 parameters

(in d the 0's are in the last position)

Cofactors (*concluding*)

Work in cofactors

1 $O(N^3)$

2 $2N^4$

3 $6N^6$

- *generating ≈ using*
- *1/2 in VBSCF*
- *3 only for Ψ_0 (gradients)*

See also

- Lowdin
- van Montfort
- Ria Braam
- Gallup
- Leisure/Balint-Kurti
- Raimondi
- Balint-Kurti
- Prosser/Hagstrom
- Malmquist

See a friendly mathematician:
W. van der Kallen / S van Edixhoven
(mathematical institute, Utrecht)

Generalised Slater rules (nonsingular)

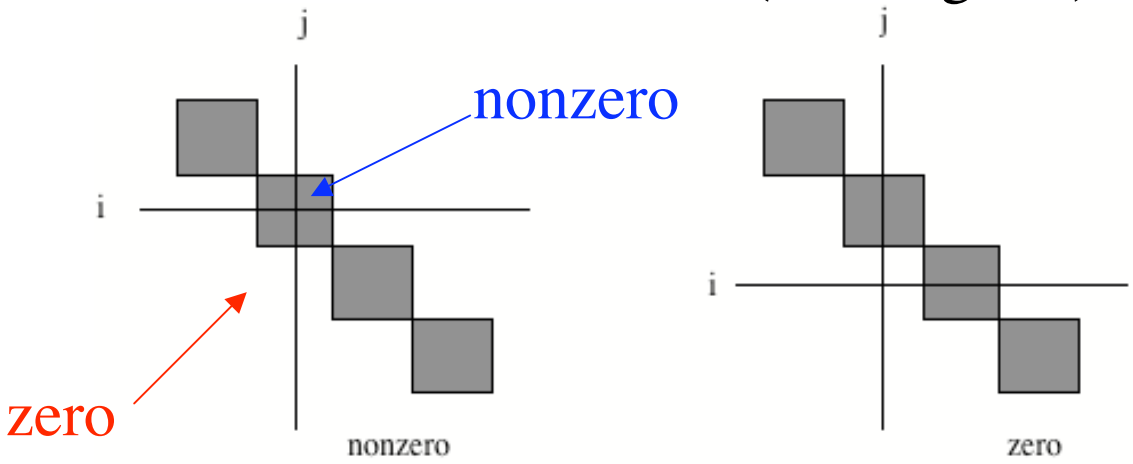


fig.1 Symbolic representation of first order cofactors of block-diagonal nonsingular matrices

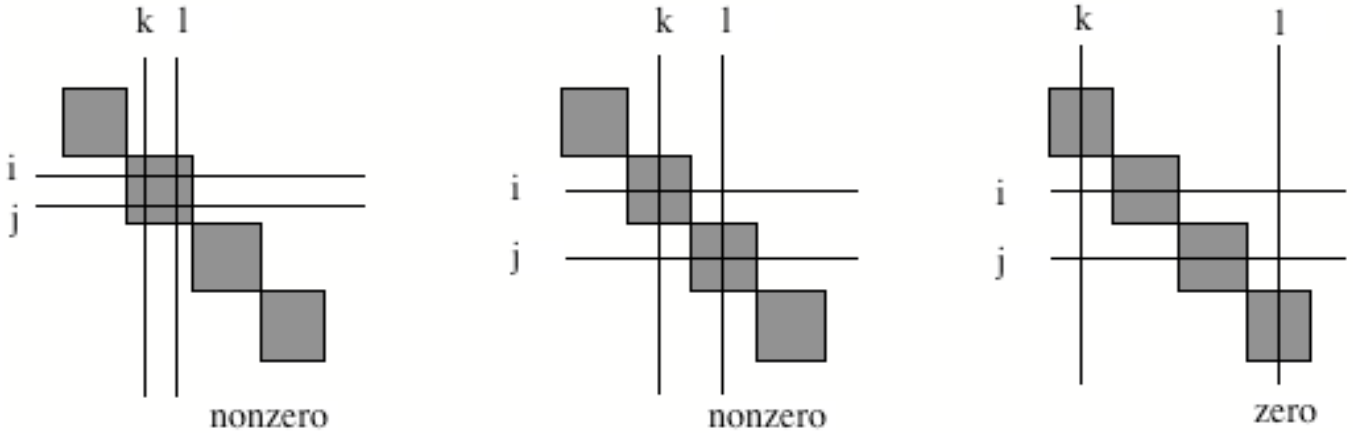


fig.2 Symbolic representation of second order cofactors of block-diagonal nonsingular matrices

Generalised Slater rules (singular)

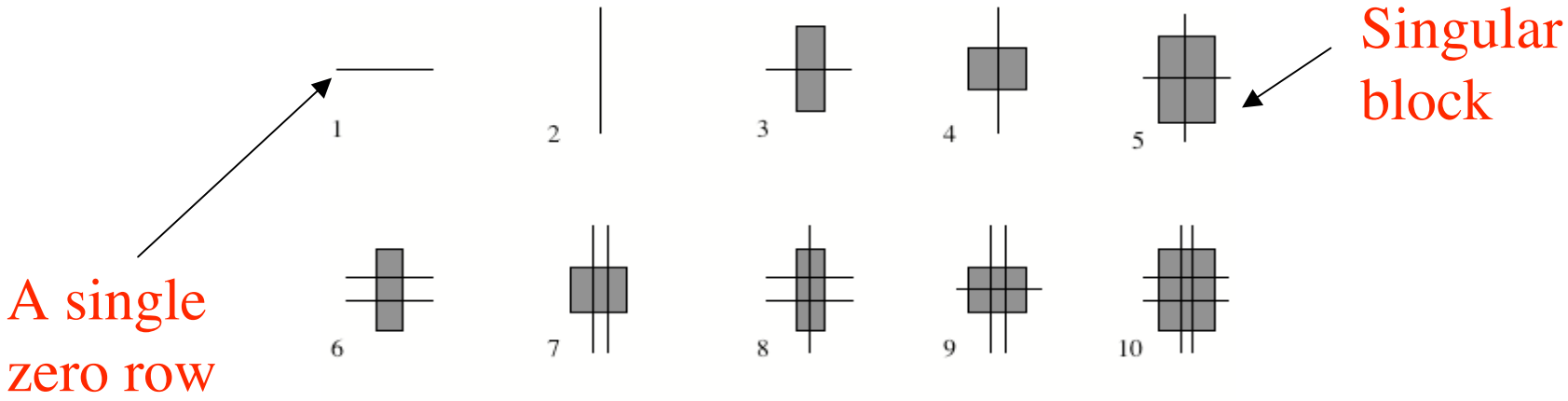


fig.3 Ten basic shapes in singular block-diagonal matrices

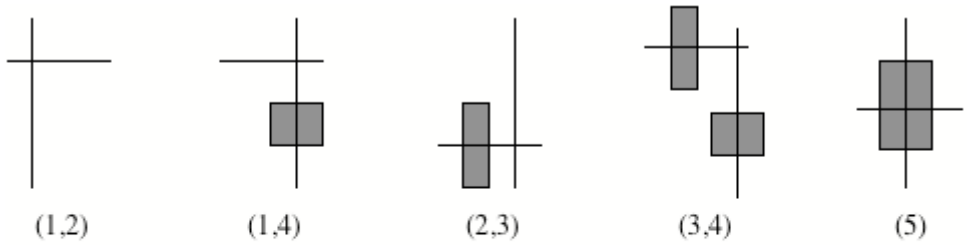


fig.4 The five cases of singly singular block-diagonal matrices

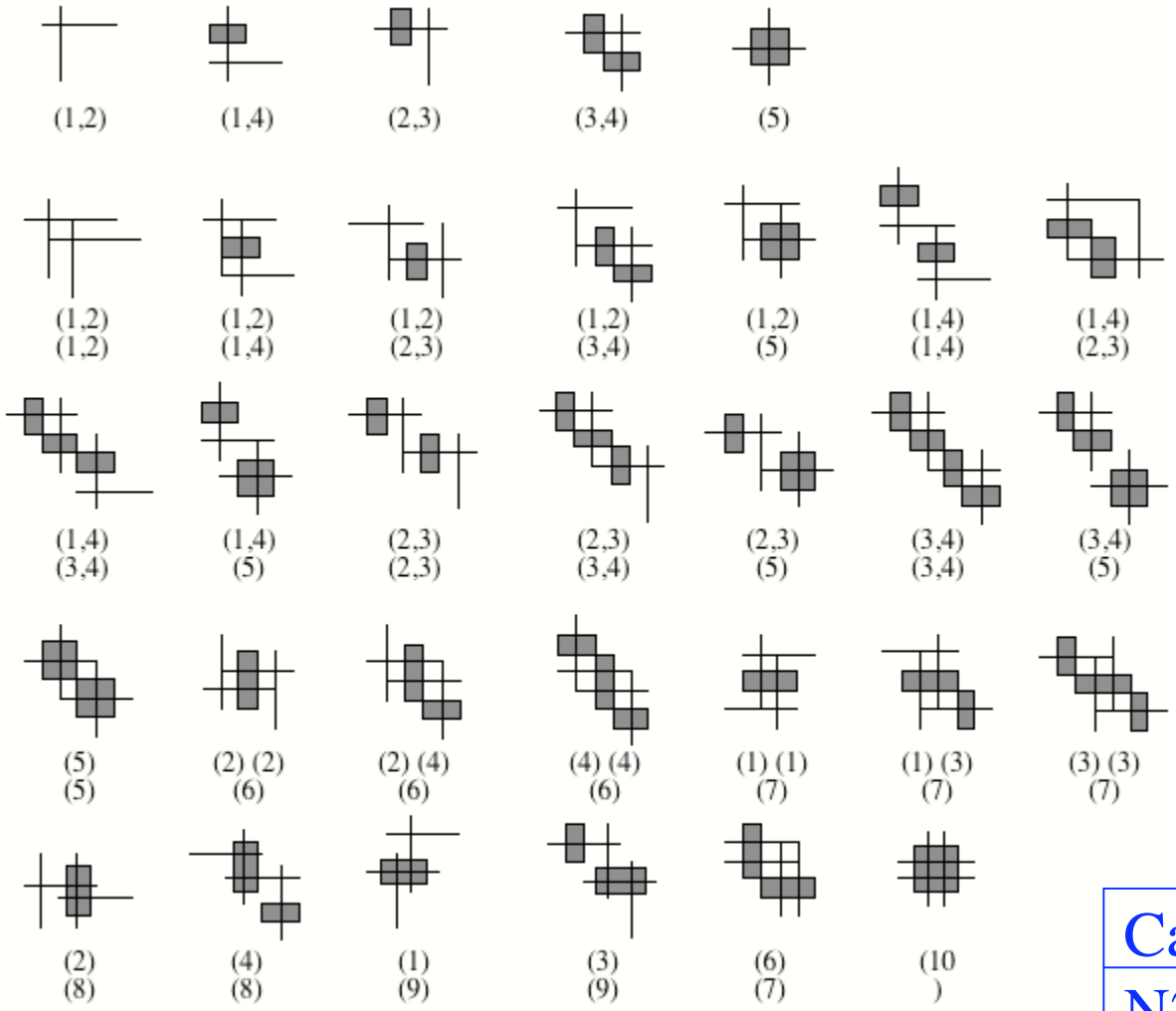


fig.5 Symbolic representation of the generalised Slater-Condon rules.
Case(0) does not have a symbol

- *Doubly's block*
- *Symmetry blocks*

Spin

- *blocks*
- *skip zero exchange*
- *no different rows/cols*

Sign was a nightmare

Timings (s)

Calculation	simple	blocks
N2 local	447	173
N2 delocal	1353	188
C3H5 deloc	8500	413