

# Evaluating matrix elements over Slater Determinants: The Slater rules.

Formulation of the problem:

Given a set of orthonormal spin-orbitals  $\psi_a, \psi_b, \dots, \psi_M$  we can construct determinants

$$\begin{aligned} \text{eg: } |\psi_a \psi_b \psi_c \psi_d| &= -|\psi_a \psi_b \psi_d \psi_c| \\ &= +|\psi_a \psi_d \psi_b \psi_c| \\ &= |K\rangle \end{aligned}$$

~~Q~~

We want to evaluate

$$\langle K | L \rangle \quad \text{and} \quad \langle K | \hat{H} | L \rangle = \langle K | \hat{h} | L \rangle + \langle K | \hat{V} | L \rangle$$

We will use antisymmetrizer  $\hat{A}$  to define determinant

$$\hat{A}^\dagger = \hat{A}$$

$$\hat{A} \hat{A} = N! \hat{A} = \hat{A}^\dagger \hat{A} = N! \hat{A}^\dagger$$

$$\hat{A} = \sum_{P \in S_N} (-1)^P \hat{P}$$

Normalized basis states

$$|K\rangle = \frac{1}{\sqrt{N!}} \hat{A} (\psi_a(1) \psi_b(2) \dots \psi_N(N))$$

Let us prove this:

$$\begin{aligned}
\langle k | k \rangle &= \frac{1}{\sqrt{H!}} \frac{1}{\sqrt{H!}} \langle \hat{A}(\psi_a \dots \psi_c) | \hat{A}(\psi_a \dots \psi_c) \rangle \\
&= \frac{1}{H!} \langle \psi_a^{(1)} \dots \psi_c^{(H)} | \hat{A}^\dagger \hat{A}(\psi_a^{(1)} \dots \psi_c^{(H)}) \rangle \\
&= \frac{1}{H!} H! \langle (\psi_a^{(1)} \dots \psi_c^{(H)}) | \hat{A}^\dagger (\psi_a^{(1)} \dots \psi_c^{(H)}) \rangle \\
&= 1 \cdot \langle \hat{A}(\psi_a^{(1)} \dots \psi_c^{(H)}) | \psi_a^{(1)} \dots \psi_c^{(H)} \rangle \\
&= \int \mathcal{D}x \sum_i (-)^{P_i} \hat{P}_i^\dagger(\psi_a^{(1)} \dots \psi_c^{(H)}) \cdot (\psi_a^{(1)} \dots \psi_c^{(H)}) \\
&\quad d_1 d_2 \dots d_H \\
&= \int \psi_a^{(1)*} \psi_b^{(2)*} \dots \psi_c^{(H)*} \psi_a^{(1)} \psi_b^{(2)} \dots \psi_c^{(H)} d\tau \\
&\quad - \int \psi_b^{(1)*} \psi_a^{(2)*} \dots \psi_c^{(H)*} \psi_a^{(1)} \psi_b^{(2)} \dots \psi_c^{(H)} d\tau \\
&\quad + \int \psi_c^{(1)*} \psi_b^{(2)*} \psi_a^{(3)*} \dots \psi_c^{(H)} \psi_a^{(1)} \dots \psi_c^{(H)} d\tau \\
&\quad \dots = 1
\end{aligned}$$

Only the identity permutation contributes; otherwise mismatch.

$$= \langle a | a \rangle \langle b | b \rangle \dots \langle c | c \rangle = 1$$

$$= \langle k | k' \rangle \quad k' \text{ differs by one orbital}$$

$$|k\rangle = |\psi_a \psi_b \dots \psi_c|$$

$$|k'\rangle = |\psi_p \psi_b \dots \psi_c|$$

→ Every thing works as before:  
Mismatch in  $b, c, d, \dots$  unless  
identity permutation

$$\langle k | k' \rangle = \langle a | p \rangle \cdot 1 \cdot 2 \cdot 1 = \langle a | p \rangle = \delta_{ap} = 0$$

$k = k'$

Important: Define determinants  
 $k$  and  $k'$  to have maximum  
coincidence: line up the orbitals  
they have in common. Put  
their differences in same, e.g. first spot.

Let us use similar technique to  
obtain other matrix elements, if  $\hat{H}$

Preliminaries:

$$\begin{aligned} & \frac{1}{N!} \langle \hat{A}(\psi_a^{(1)} - \psi_2^{(1)}) | \hat{H} | \hat{A}(\psi_a - \psi_2) \rangle \\ &= \frac{1}{N!} \langle \psi_a^{(1)} - \psi_2^{(1)} | \hat{A}^+ \hat{H} \hat{A} | \psi_a - \psi_2 \rangle \\ &= \frac{1}{N!} \langle \psi_a - \psi_2 | \hat{A}^+ \hat{H} | \psi_a - \psi_2 \rangle \\ &= \langle \psi_a - \psi_2 | \hat{A}^+ \hat{H} | \psi_a - \psi_2 \rangle \\ &= \langle \hat{A}(\psi_a^{(1)} - \psi_2^{(1)}) | \hat{H} | \psi_a - \psi_2 \rangle \end{aligned}$$

This is true for any operator  
 $\hat{H} \rightarrow \hat{O}$ , which is symmetric in  
electron labels, i.e. Any operator  
in electronic structure theory.

$$[\hat{A}, \hat{O}] = 0$$

$$\begin{aligned}
\langle k | k \rangle &= \frac{1}{\sqrt{H!}} \frac{1}{\sqrt{H!}} \langle \hat{A}(\psi_a \dots \psi_b) | \hat{A}(\psi_a \dots \psi_b) \rangle \\
&= \frac{1}{H!} \langle \psi_a^{(1)} \dots \psi_b^{(H)} | \hat{A}^\dagger \hat{A}(\psi_a^{(1)} \dots \psi_b^{(H)}) \rangle \\
&= \frac{1}{H!} H! \langle (\psi_a^{(1)} \dots \psi_b^{(H)}) | \hat{A}^\dagger (\psi_a^{(1)} \dots \psi_b^{(H)}) \rangle \\
&= 1 \cdot \langle \hat{A}(\psi_a^{(1)} \dots \psi_b^{(H)}) | \psi_a^{(1)} \dots \psi_b^{(H)} \rangle \\
&= \int \mathcal{D}\psi \sum_i (-)^{P_i} \hat{P}_i^\dagger(\psi_a^{(1)} \dots \psi_b^{(H)}) \cdot (\psi_a^{(1)} \dots \psi_b^{(H)}) \\
&\quad d\psi_1 d\psi_2 \dots d\psi_H \\
&= \int \psi_a^{(1)*} \psi_b^{(2)*} \dots \psi_b^{(H)*} \psi_a^{(1)} \psi_b^{(2)} \dots \psi_b^{(H)} d\tau \\
&\quad - \int \psi_b^{(1)*} \psi_a^{(2)*} \dots \psi_b^{(H)*} \psi_a^{(1)} \psi_b^{(2)} \dots \psi_b^{(H)} d\tau \\
&\quad + \dots \\
&= 1
\end{aligned}$$

Only the identity permutation contributes; otherwise mismatch.

$$= \langle a | a \rangle \langle b | b \rangle - \langle b | a \rangle \langle a | b \rangle = 1$$

$$= \langle k | k' \rangle \quad k' \text{ differs by one orbital}$$

$$|k\rangle = |\psi_a \psi_b \dots \psi_c|$$

$$|k'\rangle = |\psi_p \psi_b \dots \psi_c|$$

→ Every thing works as before:  
Mismatch in b, c, d, -- unless  
identity permutation

$$\langle k | k' \rangle = \langle a | p \rangle \cdot 1 \cdot 1 \cdot 1 = \langle a | p \rangle = \delta_{ap} = 0$$

$k = k'$

Important: Define determinants  
 $k$  and  $k'$  to have maximum  
coincidence: line up the orbitals  
they have in common. Put  
their differences in same, e.g. first spot.

Let us use similar technique to  
obtain other matrix elements, of  $\hat{H}$

$$\begin{aligned} \text{Preliminaries: } & \frac{1}{N!} \langle \hat{A}(\psi_a^{(1)} \psi_b^{(2)}) | \hat{H} | \hat{A}(\psi_a - \psi_b) \rangle \\ &= \frac{1}{N!} \langle \psi_a^{(1)} - \psi_b^{(2)} | \hat{A}^+ \hat{H} \hat{A} | \psi_a^{(1)} - \psi_b^{(2)} \rangle \\ &= \frac{1}{N!} \langle \psi_a - \psi_b | \hat{A}^+ \hat{H} \hat{A} | \psi_a - \psi_b \rangle \\ &= \langle \psi_a - \psi_b | \hat{A}^+ \hat{H} | \psi_a - \psi_b \rangle \\ &= \langle \hat{A}(\psi_a^{(1)} - \psi_b^{(2)}) | \hat{H} | \psi_a - \psi_b \rangle \end{aligned}$$

This is true for any generator  
 $\hat{A} \rightarrow \hat{G}$ , which is symmetric in  
electron labels; i.e. Any generator  
in electronic structure theory.

$$[\hat{A}, \hat{G}] = 0$$

Evaluate one-electron matrix elements

a) diagonal:  $\langle k | \hat{h} | k \rangle =$

$$\langle A (\psi_a(1) - \psi_b(1)) [h(1) + h(2) + \dots h(N)] \psi_a(1) - \psi_b(1) \rangle$$

$$= \langle a | h | a \rangle, \langle b | h | b \rangle, \dots \langle c | h | c \rangle - \langle b | h | a \rangle, \dots$$

$$+ \langle a | h | a \rangle, \langle b | h | b \rangle, \dots \langle c | h | c \rangle - \langle b | h | a \rangle, \dots$$

$$= \sum_{i \in k} \langle i | h | i \rangle$$

Only identity permutation contributes  
otherwise mismatch in overlap.

e.g. 2 electrons

$$\int (a(1)b(2) - b(1)a(2)) [h(1) + h(2)] a(1)b(2)$$

$$= \langle a | h | a \rangle, \langle b | h | b \rangle + \langle a | a \rangle, \langle b | h | b \rangle$$

$$- \langle b | h | a \rangle, \langle a | b \rangle - \langle b | a \rangle, \langle a | h | b \rangle$$

$$= \langle a | h | a \rangle + \langle b | h | b \rangle$$

b) Single Mismatch:  $\langle k' | \hat{h} | k \rangle$

$$\langle A (\psi_p \psi_b - \psi_q) | (h(1) + \dots h(N)) | \psi_a - \psi_c \rangle$$

$$= \langle p | h | a \rangle \langle b | b \rangle - \langle q | q \rangle$$

$$+ \langle p | a \rangle \langle b | h | b \rangle \cdot 1 + \langle q | a \rangle \langle c | h | c \rangle \cdot 2$$

$$\Rightarrow \langle k' | \hat{h} | k \rangle = \langle p b c \dots | \hat{h} | a b c \rangle$$

$$= \langle p | \hat{h} | a \rangle$$

$$= \text{Double mismatch: } \langle k'' | \hat{h} | k \rangle$$

$$= \langle A(p q c d \dots z) | \hat{h} | a b c d \dots z \rangle$$

$$p, q \neq a, b$$

$$= \langle p | \hat{h} | a \rangle \langle q | b \rangle + \langle p | b \rangle \langle q | \hat{h} | a \rangle$$

$$- \langle q | \hat{h} | a \rangle \langle p | b \rangle - \langle q | a \rangle \langle p | \hat{h} | b \rangle = 0$$

Second term from permutation:  $p \leftrightarrow q$

There is at least one mismatch in orbital overlaps:  $\langle k'' | \hat{h} | k \rangle = 0$

Summary: overlap ~~and~~  $\hat{h}$  terms

$$\langle k | \hat{h} | k \rangle = \sum_{i \in |k\rangle} \langle i | \hat{h} | i \rangle$$

$$\langle k' | \hat{h} | k \rangle = \langle p | \hat{h} | a \rangle \quad \begin{matrix} p \neq a, & (a \notin |k'\rangle) \\ p \in |k'|, & a \in |k\rangle \end{matrix}$$

$$\langle k'' | \hat{h} | k \rangle = \langle k'' | \hat{h} | k \rangle = 0$$



## Matrix elements of 2-electron operator

Let us first consider 2-electron system

$$\langle L | \hat{V} | K \rangle = \langle \hat{A}(\psi_p^{*(1)} \psi_q^{*(2)}) | \hat{V} | \psi_a^{(1)} \psi_b^{(2)} \rangle$$

$$= \int (\psi_p^{*(1)} \psi_q^{*(2)} \left( \frac{1}{r_{12}} - \psi_f^{*(1)} \psi_f^{*(2)} \right) \frac{1}{r_{12}} \psi_a^{(1)} \psi_b^{(2)} d_1 d_2$$

$$= \langle pq | \frac{1}{r_{12}} | ab \rangle - \langle qf | \frac{1}{r_{12}} | ab \rangle$$

$\equiv$  in quantum chemistry notation

$$\equiv \langle pq | ab \rangle - \langle qf | ab \rangle$$

( $\frac{1}{r_{12}}$  is implied)

$$\equiv \langle pq || ab \rangle$$

$\rightarrow$  double bar indicates antisymmetrized 2-electron integral

$$\langle pq || ab \rangle = \langle pq | ab \rangle - \langle qp | ab \rangle$$

$$\begin{aligned} \langle pq || ab \rangle &= -\langle qp || ab \rangle = +\langle qp || ba \rangle \\ &= -\langle pq || ba \rangle \end{aligned}$$

if orbitals are real:

$$= \langle ab || pq \rangle = -\langle ba || pq \rangle = -\langle ab || qp \rangle = \langle ba || qp \rangle$$

$$\Rightarrow \langle pq || ab \rangle = \langle pq | ab \rangle - \langle qp | ba \rangle$$



General treatment:  $\hat{V} = \sum_{i,j} \frac{1}{r_{ij}} = V_{12} + V_{13} + V_{23} + \dots$

Sum over all pairs.

= diagonal term  $\langle k | \hat{V} | k \rangle$

$\langle A(\psi_a \psi_b \dots \psi_c) | \left[ \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} + \dots \right] | \psi_a \psi_b \dots \psi_c \rangle$

=  $\langle ab || ab \rangle_{12} \langle c | c \rangle - \langle c | c \rangle$

+  $\langle ac || ac \rangle_{13} \langle b | b \rangle - \langle b | b \rangle$

+  $\langle bc || bc \rangle \langle a | a \rangle - \langle a | a \rangle$

+ ...

=  $\sum_{i,j \in k} \langle ij || ij \rangle$  (sum over all distinct pairs)

= Single mismatch:  $\langle k' | V | k \rangle$

=  $\langle A(\psi_p \psi_b \dots \psi_c) | \hat{V} | \psi_a \psi_b \dots \psi_c \rangle$

=  $p$  and  $a$  must be in  $\psi$

otherwise overlap mismatch

→ only  $V_{12}, V_{13}, V_{14}, \dots$  contribute,  
not  $V_{23}, \dots$  etc.

$\langle k' | V | k \rangle = \langle p || ab \rangle + \langle p || ac \rangle + \dots \langle p || az \rangle$

=  $\sum_{i \in k, \substack{a \\ k'}} \langle p || ai \rangle$

finally double mismatch:  $\langle k'' | V | k \rangle$

$$\langle A(\psi_p \psi_q \psi_c - \psi_c) | \hat{V} | \psi_a \psi_b - \psi_c \rangle$$

only  $\frac{1}{r_{12}}$  contributes

$$\langle pq || ab \rangle \langle c | c \rangle - \langle c | c \rangle = \langle pq || ab \rangle$$

Summary all matrix-elements

$$\begin{array}{ccc} \langle k | H | k \rangle & \frac{\sum_{a \in k} \langle a | \hat{h} | a \rangle}{k} & \sum_{\substack{a, b \\ \in k}} \langle ab || ab \rangle \end{array}$$

$ab \sim z$        $ab \sim z$

$$\begin{array}{ccc} \langle k' | H | k \rangle & \langle p | \hat{h} | a \rangle & \sum_{b \in k, k'} \langle pb || ab \rangle \end{array}$$

$pb \sim z$        $ab \sim z$

$$\begin{array}{ccc} \langle k'' | H | k \rangle & 0 & \langle pq || ab \rangle \end{array}$$

$pqc \sim z$        $abc \sim z$

$$\begin{array}{ccc} \langle k''' | H | k \rangle & 0 & 0 \end{array}$$

Sum over all contributions that include the special (differing) orbitals in the two determinants

Signs: Bring determinants into maximum coincidence first.

To evaluate matrix elements  
 $\langle K | \hat{H} | L \rangle$  we only require

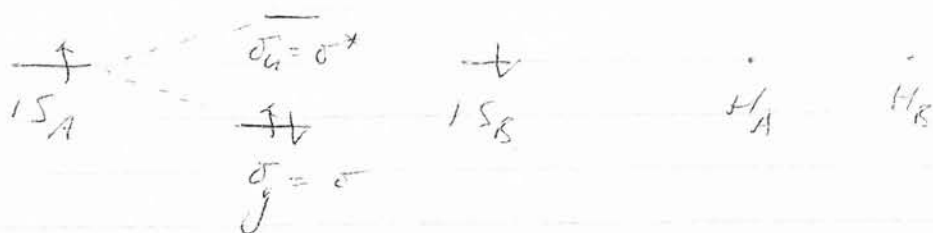
one- and two-electron integrals,  
 no matter how many electrons we have

$$\begin{array}{ll} \langle p | \hat{h} | q \rangle & \frac{1}{2} M^2 \\ \langle pq || rs \rangle & \frac{1}{8} M^4 \end{array} \rightarrow \text{computable (still large \#)}$$

We typically cannot store  
 Hamiltonian  $\langle K | \hat{H} | L \rangle$   
 or all determinants  $\frac{1}{2} \begin{pmatrix} M \\ N \end{pmatrix}^2$ .

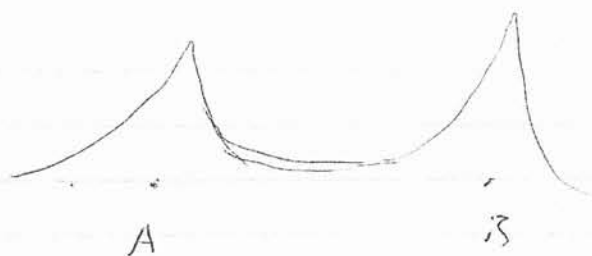
Let us look at examples first.

prototypical example:  
 $H_2$  in a minimal basis set

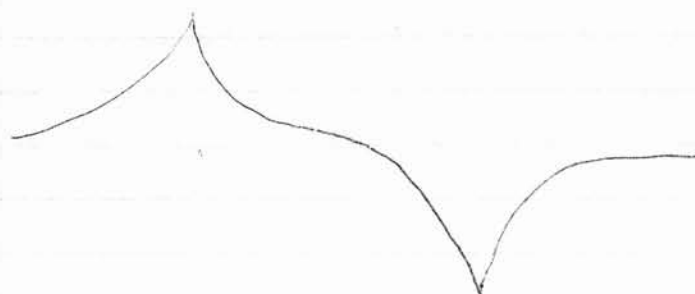


$$\sigma_g: (1s_A + 1s_B) \cdot \frac{1}{\sqrt{2(1+S)}}$$

$$\sigma_u: (1s_A - 1s_B) \cdot \frac{1}{\sqrt{2(1-S)}}$$



bonding  
 $\sigma_g$  orbital



antibonding  
 $\sigma_u$  orbital

Molecular orbital theory:  
put both electrons in bonding  
orbital

(2) —

(1)  $\uparrow\downarrow$

$|1\bar{1}\rangle$

Configuration interaction:  
true wfn (in minimal basis)  
is linear combination

$$c_1 |\bar{\sigma}_g \bar{\sigma}_g\rangle + c_2 |\bar{\sigma}_u \bar{\sigma}_u|$$

$$= c_1 |1\bar{1}\rangle + c_2 |2\bar{2}|$$

(The other determinants  
 $|\bar{\sigma}_g \bar{\sigma}_u|$  and  $|\bar{\sigma}_u \bar{\sigma}_g|$  have  
wrong symmetry:  $g \times u = u$ )

In CI: create Hamiltonian matrix  $\langle \lambda | H | \mu \rangle$

$H$	$ 1\bar{1}\rangle$	$ 2\bar{2}\rangle$
$\langle 1\bar{1} $	$\langle 1 h 1\rangle + \langle \bar{1} h \bar{1}\rangle + \langle 1\bar{1}  1\bar{1}\rangle$	$\langle 1\bar{1}  2\bar{2}\rangle$
$\langle 2\bar{2} $	$\langle 2\bar{2}  1\bar{1}\rangle$	$\langle 2 h 2\rangle + \langle \bar{2} h \bar{2}\rangle + \langle 2\bar{2}  2\bar{2}\rangle$

$$= \begin{bmatrix} \epsilon_1 & V \\ V & \epsilon_2 \end{bmatrix}$$

Energies:  $\begin{vmatrix} \epsilon_1 - \lambda & V \\ V & \epsilon_2 - \lambda \end{vmatrix} = 0$

$$(\epsilon_1 - \lambda)(\epsilon_2 - \lambda) - V^2 = 0$$

$$\epsilon_1 \epsilon_2 - \lambda(\epsilon_1 + \epsilon_2) + \lambda^2 - V^2 = 0$$

$$\lambda = \frac{1}{2}(\epsilon_1 + \epsilon_2 \pm \sqrt{(\epsilon_1 + \epsilon_2)^2 - 4[(\epsilon_1 \epsilon_2) - V^2]})$$

$$= \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \frac{1}{2}\sqrt{(\epsilon_1 - \epsilon_2)^2 + 4V^2}$$

$$\approx \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \left( \frac{1}{2}(\epsilon_1 - \epsilon_2) + \frac{V^2}{(\epsilon_1 - \epsilon_2)} \right)$$

due to CI the energy levels shift from  $\epsilon_1$  and  $\epsilon_2$



due to CI

The shift depends on  
 $V = \langle 1T || 2\bar{2} \rangle$

and  $(\epsilon_1 - \epsilon_2) \propto \frac{V^2}{\epsilon_1 - \epsilon_2} \ll 0$

We will analyse this prototypical molecule in more detail later on. (see handout)

For now: CI (diagonalize the matrix) is the correct result

at long distance  $\epsilon_1 \approx \epsilon_2$

Second-order correction  $\frac{V^2}{\epsilon_1 - \epsilon_2} \rightarrow -\infty$ !

This is behaviour of MP2.  
 (in Gaussian).

Other prototypical examples:

Single excited states  
Homo-Lumo excitation



$$E_T = \langle 1|h|1 \rangle + \langle 2|h|2 \rangle + \langle 12||12 \rangle$$

to calculate singlet energy  
set up the  $2 \times 2$  matrix

	$ 1\bar{2}\rangle$	$ T2\rangle$
$\langle 1\bar{2} $	$\langle 1 h 1 \rangle + \langle 2 h 2 \rangle + \langle 1\bar{2}  1\bar{2} \rangle$	$\langle 1\bar{2}  T2 \rangle$
$\langle T2 $	$\langle T2  1\bar{2} \rangle$	$\langle 1 h T \rangle - \langle 2 h 2 \rangle + \langle T2  T2 \rangle$

what can we say about the integrals in terms of the spin-orbitals?

Let us assume that the spatial parts of the orbitals are the same  $|1\rangle = \varphi_1(\vec{r})|\uparrow\rangle$   $|T\rangle = \varphi_1(\vec{r})|\uparrow\rangle$



$$\langle 1\bar{2} || 1\bar{2} \rangle = \langle 1\bar{2} | 1\bar{2} \rangle - \langle 1\bar{2} | 2\bar{1} \rangle$$

$$= \int \psi_1(1) \bar{\psi}_2(2) \frac{1}{r_{12}} \psi_1(1) \bar{\psi}_2(2) d_1 d_2$$

$$- \int \psi_1(1) \bar{\psi}_2(2) \frac{1}{r_{12}} \bar{\psi}_2(1) \psi_1(2) d_1 d_2$$

The second integral is zero because the spin does not match

$$\langle 20 || \beta\alpha \rangle = 0$$

On the other hand:

$$\langle 1\bar{2} || T\bar{2} \rangle = \langle 1\bar{2} | T\bar{2} \rangle - \langle 1\bar{2} | 2T \rangle$$

$$= 0 - \langle 12 | 21 \rangle$$

(spatial integral.)

because these integrals occur often they get a special symbol

$$\langle ab | ab \rangle = J_{ab} ; \langle 12 | 12 \rangle = J_{12}$$

$$\langle ab | ba \rangle = K_{ab} \quad \langle 12 | 21 \rangle = K_{12}$$

Moreover

$$\langle a | h | a \rangle = \langle \bar{a} | h | \bar{a} \rangle = h_{aa}$$

then CI matrix reduces to

$$\begin{array}{c|cc}
 & |1\bar{2}\rangle & |\bar{1}2\rangle \\
 \hline
 \langle 1\bar{2}| & h_{11} + h_{22} + J_{12} & -K_{12} \\
 \langle \bar{1}2| & -K_{12} & h_{11} + h_{22} + J_{12}
 \end{array}$$

$$= \begin{bmatrix} \epsilon_a & -K_{12} \\ -K_{12} & \epsilon_b \end{bmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = (\epsilon_1 - K_{12}) \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\begin{bmatrix} \epsilon_b & -K_{12} \\ -K_{12} & \epsilon_a \end{bmatrix} \begin{pmatrix} 1 \\ -1 \end{pmatrix} = (\epsilon_1 + K_{12}) \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Compare to triplet energy

$$\begin{aligned}
 & h_{11} + h_{22} + \langle 12 || 12 \rangle \\
 & = h_{11} + h_{22} + J_{12} - K_{12} \\
 & = \epsilon_b - K_{12}
 \end{aligned}$$

hence  $|1\bar{2}\rangle + |\bar{1}2\rangle$  : triplet state

$$\hat{S}_- |12\rangle = |1\bar{2}\rangle + |\bar{1}2\rangle \quad E = \epsilon_1 - K_{12}$$

$$|1\bar{2}\rangle - |\bar{1}2\rangle \quad \text{Singlet state}$$

$$E_{\text{singlet}} = E_h + K_{12}$$

$$\hat{S}_+ (|1\bar{2}\rangle - |\bar{1}2\rangle) = |12\rangle - |12\rangle = 0$$

$$\begin{aligned} \text{The integral } \int \psi_1(r_1) \psi_2(r_2) \frac{1}{r_{12}} \psi_2(r_1) \psi_1(r_2) \\ = K_{12} > 0 \end{aligned}$$

hence in this  $2 \times 2$  model

$$E_{\text{singlet}} > E_{\text{triplet}}$$

$$\text{splitting is } 2 \times K_{12}$$

$K_{12}$  is called the exchange interaction.

This is the origin of Hund's rule in atomic spectra.

parallel spins are favoured (other things being equal) lower in energy because

exchange interaction due to antisymmetry of wave function.

Using the Slater rules  
we can easily write down  
the energy expression for  
any determinant

$$\text{eg: } \begin{array}{cc} \uparrow & 3 \\ \uparrow & 2 \\ \uparrow\downarrow & 1 \end{array} \quad \begin{array}{c} 3 \\ 2 \\ 1 \end{array}$$

$\langle h|h \rangle$

$$E = \langle 1|h|1 \rangle + \langle \bar{1}|h|\bar{1} \rangle + \langle 2|h|2 \rangle + \langle 3|h|3 \rangle$$

$$+ \langle \bar{1}|\bar{1}|\bar{1} \rangle + \langle 1|2|12 \rangle + \langle 1\bar{1}|\bar{1}\bar{1} \rangle$$

$$+ \langle \bar{1}2|\bar{1}2 \rangle + \langle \bar{1}\bar{1}|\bar{1}\bar{1} \rangle + \langle 23|23 \rangle$$

all pairs.

$$\text{or: } \begin{array}{cc} \uparrow\downarrow & 2\bar{2} \\ \uparrow\downarrow & 1\bar{1} \end{array}$$

$$E = \langle 1|h|1 \rangle + \langle \bar{1}|h|\bar{1} \rangle + \langle 2|h|2 \rangle + \langle \bar{2}|h|\bar{2} \rangle$$

$$+ \langle 1\bar{1}|\bar{1}\bar{1} \rangle + \langle 12|12 \rangle + \langle 1\bar{2}|\bar{1}\bar{2} \rangle$$

$$+ \langle \bar{1}2|\bar{1}2 \rangle + \langle \bar{1}\bar{2}|\bar{1}\bar{2} \rangle + \langle \bar{2}2|2\bar{2} \rangle$$

easy enough, but a bit tedious!

Same as:  $\sum_{a \leq b} \langle ab|a \rangle + \sum_{a \leq b} \langle ab|b \rangle$

Library

Let us condense a little bit and consider spin explicitly.

Assume same spatial orbitals for  $\alpha$  and  $\beta$  spin.

Consider also real orbitals only.

$$\langle a|h|\bar{a} \rangle = \langle \bar{a}|h|a \rangle = h_{aa}$$

$$\langle a|h|\bar{b} \rangle = 0$$

$$\langle a b | a b \rangle = J_{ab} \quad (\text{spatial Coulomb integral})$$

$$\langle a b | b a \rangle = K_{ab} \quad (\text{exchange integral})$$

$$J_{ab} = \int \psi_a^*(1) \psi_a(1) \frac{1}{r_{12}} \psi_b^*(2) \psi_b(2) d1 d2$$

Coulomb interaction between densities  $|\psi_a(1)|^2$  and  $|\psi_b(2)|^2$

$$K_{ab} = \int \psi_a^*(1) \psi_b(1) \frac{1}{r_{12}} \psi_a(2) \psi_b(2) d1 d2$$

Coulomb between distribution

$\psi_a(1) \psi_b(1)$  and  $\psi_a(2) \psi_b(2)$   
 $\psi_a \psi_b$  may not be positive everywhere

but  $K_{ab} > 0$  always.

We would have more integrals  $\langle pq | rs \rangle$ , but in the examples

we discuss, we can use the 'diagonal' integrals, exclusively.

$$\langle ab || ab \rangle = J_{ab} - K_{ab}$$

$$\langle a\bar{b} || a\bar{b} \rangle = J_{ab}$$

$$\begin{aligned} \langle a\bar{b} || \bar{a}b \rangle &= - \langle a\bar{b} || b\bar{a} \rangle = -K_{ab} \\ &\quad \text{(line up the spins)} \\ &= - \langle \overset{1}{a} \overset{2}{\bar{b}} || \overset{1}{b} \overset{2}{\bar{a}} \rangle \end{aligned}$$

Moreover because the integrals/orbitals are real:

$$\langle a \overset{1}{a} | \overset{2}{b} \overset{1}{b} \rangle = \langle a b | b a \rangle = K_{ab}$$

$$\langle a \bar{a} || b \bar{b} \rangle = K_{ab}$$

Using these integrals we can set up some interesting problems.

## Return to atoms

"2-electron" system  $1s^2 2s^2 (2p)^2$   
Carbon atom.

We know from angular momentum theory  $\frac{6 \times 5}{2} = 15$  states

$$|P_1 \bar{P}_1| \rightarrow {}^1D \quad 5$$

$$|P_1 P_0| \rightarrow {}^3P \quad 9$$

$${}^1S$$

$$\frac{1}{15}$$

functions.

If we diagonalize the full  $H$  over 15 determinants we should get precisely this degeneracy pattern  $15 \times 15$   $H$  ! too much

Let us analyse the problem, cutting it up in smaller pieces.

We will use real orbitals

$$P_x, P_y, P_z, \bar{P}_x, \bar{P}_y, \bar{P}_z$$

→ abbreviate further  $x, y, z, \bar{x}, \bar{y}, \bar{z}$

$$M_S = 0 \text{ functions } \begin{cases} x\bar{x}, y\bar{y}, z\bar{z} \\ x\bar{y}, x\bar{z}, y\bar{z}, y\bar{x}, z\bar{x}, z\bar{y} \end{cases}$$

$$M_S = 1: x y, x z, y z$$

$$M_S = -1: \bar{x} \bar{y}, \bar{x} \bar{z}, \bar{y} \bar{z}$$



Types of 2-electron integrals:

$$h_{xx} = h_{yy} = h_{zz} \equiv h$$

$$\langle xx | xx \rangle = \langle yy | yy \rangle = \langle zz | zz \rangle = D$$

$$\langle xy | xy \rangle = \langle xz | xz \rangle = \langle yz | yz \rangle = J$$

$$\langle xy | yx \rangle = \langle xz | zx \rangle = \langle yz | zy \rangle = K$$

$$\langle xx | yy \rangle = \langle xx | zz \rangle = \langle yy | zz \rangle = K$$

$$\text{also } \langle ab | cd \rangle = \langle cd | ab \rangle \\ = \langle ad | cb \rangle$$

Integrals in which  $x, y, z$  occur an odd number of times are zero (odd in  $x, y, \text{ or } z \rightarrow$  odd integrand, integrates to zero)

There is one more important relation between the integrals:

$$D = J + 2K$$

How we can partition Hamiltonian in small sub-blocks.

$\begin{array}{c} \uparrow \uparrow - \\ \hline 2s \\ \hline 1s \end{array}$	<p>Contributions from interactions with <math>s</math>-electrons is the same for each <math>1s^2 2s^2</math> configuration (constant shift to <math>E</math>).</p>
--	--

$$M_S = 1$$

	$x y$	$x z$	$y z$
$x y$	$2h + j - k$	0	0
$x z$	0	$2h + j - k$	0
$y z$	0	0	$2h + j - k$

$$E(^3P) = 2h + j - k, \text{ same for } M_S = -1$$

→ no coupling between states with different  $x, y, z$  odd  $x, y, z$  in matrix-element.

$$M_S = 0$$

	$x \bar{y}$	$y \bar{x}$
$x \bar{y}$	$2h + j$	$+k$
$y \bar{x}$	$+k$	$2h + j$

$$\langle x \bar{y} | \hat{g} | x \bar{x} \rangle = + \langle x \bar{y} | y \bar{x} \rangle$$

$$\rightarrow E = 2h + j \pm k \quad (x \bar{y} + y \bar{x})$$

$$E(^3P) = 2h + j - k \quad |x \bar{y}\rangle \rightarrow |y \bar{x}\rangle$$

$$E(^1D) = 2h + j + k \quad |x \bar{y}\rangle + |y \bar{x}\rangle$$

2 more: same for  $\begin{cases} x \bar{z} \pm z \bar{x} \\ y \bar{z} \pm z \bar{y} \end{cases}$

⇒ 9 states found for  $^3P$   
3 states for singlet  $^1D$

Finally :

M	$x\bar{x}$	$y\bar{y}$	$z\bar{z}$
$x\bar{x}$	$2h + D$	$k$	$k$
$y\bar{y}$	$k$	$2h + D$	$k$
$z\bar{z}$	$k$	$k$	$2h + D$

$$\langle x\bar{x} | y\bar{y} \rangle = k$$

familiar structure Hamiltonian!  
eigenvalues, eigenvectors

$$\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}, \quad E = 2h + D + 2k \quad \begin{matrix} \uparrow \\ D = J + 2k \end{matrix}$$

$$\rightarrow 2h + J + 4k$$

$$\begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}, \begin{pmatrix} 2 \\ -1 \\ -1 \end{pmatrix} \quad E = 2h + D - k$$

$$= 2h + J + k$$

$$|s\rangle = |x\bar{x}\rangle + |y\bar{y}\rangle + |z\bar{z}\rangle$$

$$|D\rangle = \begin{cases} |y\bar{y}\rangle - |z\bar{z}\rangle & (|x\bar{x}\rangle - |y\bar{y}\rangle) \\ 2|x\bar{x}\rangle - |y\bar{y}\rangle - |z\bar{z}\rangle & 2(|z\bar{z}\rangle + |x\bar{x}\rangle - |y\bar{y}\rangle) \end{cases}$$

$$E(|D\rangle) = \begin{cases} 2h + D - k \\ 2h + J + k \end{cases} \quad \left\{ \begin{array}{l} D = J + 2k \\ \text{as mentioned} \end{array} \right.$$

$$D_{x\bar{y}}, D_{x\bar{z}}, D_{y\bar{z}}, D_{x\bar{x}-y\bar{y}}, D_{z\bar{z}} \text{ (like d-orbitals)}$$

In exercises you are asked  
to go through carbon atom,  
but also do Hydrogen atom.

Multiplet structure:

$$|P_1 P_0 P_{-1}| \rightarrow 4S^1 \quad 4$$

$$|P_1 \bar{P}_1 P_0| \rightarrow 2D \quad 10$$

$$2P \quad 6$$

20 functions

Using same notation as before  
we can guess

$$|X_4 \bar{X}_1| \rightarrow 4S^1$$

$$|X_4 \bar{X}_1|, |X_2 \bar{X}_1|, |X_2 \bar{X}_1| \rightarrow 4S^{(1)} \quad 2D^{(2)}$$

3x3 H

$$|X \bar{X}_4|, |X \bar{X}_2| \rightarrow 2P^{(3)}, 2D^{(3)}$$

(same for line 4, 2)

Same for excess down spin,  $|X \bar{X}_4|$  etc.

you will work it all out  
and see the Multiplet structure  
image.

Evaluating Expectation Values  
using  $h_{aa}$ ,  $J_{ab}$  and  $K_{ab}$  integrals

$$\langle \phi | H | \phi \rangle \rightarrow$$

$$\begin{aligned} & \sum_a h_{aa} \quad \text{Sum of 1-electron terms} \\ & + \sum_{a < b} J_{ab} \quad \text{Sum over all pairs regardless of spin} \\ & + \sum_{\substack{a < b \\ \text{like spin}}} -K_{ab} \quad \text{Sum over all pairs that have equal spin.} \end{aligned}$$

Examples:

$$\begin{array}{lcl} \uparrow & 3 & 2h_{11} + h_{22} + h_{33} \\ \uparrow & 2 & + J_{11} + 2J_{12} + 2J_{13} + J_{23} \\ \uparrow & 1 & - K_{12} - K_{13} - K_{23} \end{array}$$

$$- \quad 3$$

$$\begin{array}{lcl} \uparrow\uparrow & 2 & 2h_{11} + 2h_{22} \\ & & + J_{11} + 4J_{12} + J_{22} \\ \uparrow\uparrow & 1 & - 2K_{12} \end{array}$$

Aufbau principle:  $h_{22} < h_{33}$  wins  
from like-spin energy lowering through  
exchange

Hilroy

## Breaking the bond in $H_2$

$$\sigma_g = (1s_a + 1s_b) / \sqrt{2+2S}$$

$$\sigma_u = (1s_a - 1s_b) / \sqrt{2-2S}$$

$$S = \int 1s_a(r) 1s_b(r) dr$$

Integral rapidly becomes small

→ assume  $S = 0$ .

$1s_a(r) 1s_b(r) \approx 0$  everywhere in space.



no overlap

Molecular orbital wave function at large distance

$$\begin{aligned} |\sigma_g \bar{\sigma}_g| &= \frac{1}{2} |(a+b)(\bar{a}+\bar{b})| \\ &= \frac{1}{2} \left[ (|a\bar{a}| + |b\bar{b}|) + (|a\bar{b}| + |b\bar{a}|) \right] \\ &= \frac{1}{2} \phi_{\text{ionic}} + \frac{1}{2} \phi_{\text{covalent}} \end{aligned}$$

Equal weight ionic + covalent contributions.

→  $E |\sigma_g \bar{\sigma}_g|$  far too high at stretched R.

$$\begin{aligned}
 |\sigma_u \bar{\sigma}_u| &= \frac{1}{2} |(a-b)(\bar{a}-\bar{b})| \\
 &= \frac{1}{2} (|a\bar{a}| + |b\bar{b}| - |a\bar{b}| - |b\bar{a}|) \\
 &= \frac{1}{2} (\phi_{\text{ionic}} - \phi_{\text{covalent}})
 \end{aligned}$$

$$\begin{aligned}
 \rightarrow |\sigma_g \bar{\sigma}_g| - |\sigma_u \bar{\sigma}_u| & \quad \text{Correct in asymptote} \\
 &= \phi_{\text{covalent}} = (|a\bar{b}| + |b\bar{a}|)
 \end{aligned}$$

The linear combination with coefficient 1, -1 is proper solution in asymptote.

at all geometries a correct wave function is obtained from combination

$$\begin{aligned}
 &c_1 |\sigma_g \bar{\sigma}_g| + c_2 |\sigma_u \bar{\sigma}_u| \\
 &= \frac{1}{2} [(c_1 + c_2) \phi_{\text{ionic}} + (c_1 - c_2) \phi_{\text{covalent}}]
 \end{aligned}$$

H	$ \sigma_g \bar{\sigma}_g $	$ \sigma_u \bar{\sigma}_u $
$ \sigma_g \bar{\sigma}_g $	$2h_1 + J_{11}$	$K_{12}$
$ \sigma_u \bar{\sigma}_u $	$K_{12}$	$2h_2 + J_{22}$



To understand breaking of  
chemical bond one needs to  
do CI calculation.

The formation of chemical bond  
can be understood (at least  
qualitatively) from Molecular  
Orbital theory, using only the  
 $1 \text{ of } \bar{\sigma}_g$  determinant

Alternatively one can use the  
Heitler - London description  
for the complete potential energy  
curve

$$\begin{vmatrix} 1S_A & 1S_B \end{vmatrix} + \begin{vmatrix} 1S_B & 1S_A \end{vmatrix} \\ = \phi_{\text{covalent}}$$

Even freezing the  $1S$  orbitals at  
the atomic orbital level provides  
qualitative understanding of chemical  
bond. This would involve the  
atomic orbital Coulomb and exchange  
integrals  $J_{AB}$ ,  $K_{AB}$

Famous paper by Heitler-London  
"valence bond theory"  
advocated by Linus Pauling.  
Needs to consider non-orthogonality.