

### MATRIX ELEMENTS OF F(i) AND G(i,j)

Last time: orbitals → configurations → states (“terms”)

Fermions: Slater Determinants: Pauli Exclusion Principle

Notation for Slater Determinant: ||main diagonal||.

TODAY: 1. SLATER DETERMINANTAL MATRIX ELEMENTS

A. Normalization

B. F(i) One - e<sup>-</sup> operator e.g.  $\mathbf{H}^{SO} = \sum_i a(r_i) \ell_i \cdot \mathbf{s}_i$

C. G(i,j) Two - e<sup>-</sup> operator e.g.  $\mathbf{H}^e = \sum_{i>j} e^2 / r_{ij}$

Recall: specify standard order (because Determinant changes sign upon binary permutation)

Goal: make inconvenience of Slater determinants almost vanish — matrix elements will be almost what you expect for simple non-antisymmetrized products of spin-orbitals.

pages 31-2,3,4 are repeat of 30-6, 7,8

A. Normalization:  $|\Psi_N\rangle = (N!)^{-1/2} \sum_{\wp} (-1)^p \wp [ |u_1(1)\rangle \dots |u_N(N)\rangle ]$

verify that  $(N!)^{-1/2}$  is correct factor

$$\langle \Psi_N | \Psi_N \rangle = (N!)^{-1} \sum_{\wp, \wp'} (-1)^{p+p'} \wp [ \langle u_1(1) | \dots \langle u_N(N) | ] \wp' [ |u_1(1)\rangle \dots |u_N(N)\rangle ]$$

rearrange into products of one - e<sup>-</sup> overlap integrals:

$$= (N!)^{-1} \sum_{\wp, \wp'} (-1)^{p+p'} \prod_{i=1}^N \langle \mathbf{P}_i u_i | \mathbf{P}'_i u_i \rangle$$

\*  $|u_i\rangle$  are orthonormal

\*  $\langle u(i) | u(j) \rangle$  has no meaning because bra and ket must be associated with SAME e<sup>-</sup>

only nonzero LEGAL terms in  $\sum_{\wp, \wp'}$  are those where EACH  $\mathbf{P}_i = \mathbf{P}'_i$  otherwise get AT LEAST

\* 2 MISMATCHED bra - kets

$$\langle u_i(k) | u_j(k) \rangle \dots \langle u_j(\ell) | u_i(\ell) \rangle$$

$$= 0 \qquad = 0$$

(Here the electron names match in each bra-ket but the spin-orbitals do not match.)

Think of a one- or two-e<sup>-</sup> operator as a scheme for dealing with or “hiding” the small number of mismatched spin-orbitals.

Thus it is necessary that  $\wp = \wp'$  ,  $p = p'$  ,  $(-1)^{p+p'} = +1$   
 and  $\langle \psi_N | \psi_N \rangle = (N!)^{-1} \sum_{\wp} \wp \left[ \langle u_1(1) | u_1(1) \rangle \dots \langle u_N(N) | u_N(N) \rangle \right]$   
 $\hspace{15em} = 1 \hspace{15em} = 1$

each term in sum over  $\wp$  gives + 1, but there are N possibilities for  $P_1, N - 1$  possibilities for  $P_2$

$\therefore N!$  possibilities for sum over  $\wp$

$$\langle \psi_N | \psi_N \rangle = (N!)^{-1} \sum_{\wp} 1 = 1$$

Thus the assumed  $(N!)^{-1/2}$  normalization factor is correct.

B. Matrix elements of one-electron operators

$$\mathbf{F} = \sum_i f(\mathbf{r}_i) \quad \text{e.g.} \quad \bar{\mathbf{L}} = \sum_i \bar{\mathbf{l}}_i$$

$$|\psi_A\rangle \equiv (N!)^{-1/2} \sum_{\wp} (-1)^p \wp |a_1(1)\rangle \dots |a_N(N)\rangle$$

$$|\psi_B\rangle \equiv (N!)^{-1/2} \sum_{\wp'} (-1)^{p'} \wp' |b_1(1)\rangle \dots |b_N(N)\rangle$$

$$\begin{aligned} \langle \psi_A | \mathbf{F} | \psi_B \rangle &= (N!)^{-1} \sum_{i, \wp, \wp'} (-1)^{p+p'} \wp \left[ \langle a_1(1) | \dots \right] f(\mathbf{r}_i) \wp' \left[ | b_1(1) \rangle \dots \right] \\ &= (N!)^{-1} \sum_{i, \wp, \wp'} (-1)^{p+p'} \left[ \langle \mathbf{P}_1 a_1(1) | \mathbf{P}_1 b_1(1) \rangle \right] \\ &\quad \dots \left[ \langle \mathbf{P}_i a_i(i) | f(\mathbf{r}_i) | \mathbf{P}'_i b_i(i) \rangle \right] \dots \left[ \langle \mathbf{P}_N a_N(N) | \mathbf{P}'_N b_N(N) \rangle \right] \end{aligned}$$

Product of N orbital matrix element factors in each term of sum. Of these, N-1 are orbital overlap integrals and only *one* involves the one-e<sup>-</sup> operator.

## 5.73 Lecture #31

31 - 3

SELECTION RULE  $\langle \Psi_A | \mathbf{F} | \Psi_B \rangle = 0$  if  $|\psi_A\rangle$  and  $|\psi_B\rangle$  differ by more than one spin-orbital  
(at least one of the orbital overlap integrals would be zero)

two cases remain:

1. differ by one spin-orbital

$$\left. \begin{aligned} |\psi_A\rangle &= \|u_1(1) \dots a_k(k) \dots u_N(N)\| \\ |\psi_B\rangle &= \|u_1(1) \dots b_k(k) \dots u_N(N)\| \end{aligned} \right\} \begin{array}{l} \text{the mismatched orbitals} \\ \text{are in the same position} \end{array}$$

use  $u_i$  to denote common spin-orbitals

use  $a_k, b_k \neq 0$  to denote unique spin-orbitals

for this choice, all  $N$   $P_i$  factors of each  $\wp$  must be identical to all  $N$  factors of  $\wp'$

additional requirement:  $\wp$  must bring mismatched orbitals into  $i$ -th position  
so that they match up with the  $f(\mathbf{r}_i)$  operator to give  $\langle a_k(i) | f(\mathbf{r}_i) | b_k(i) \rangle$

ANY OTHER ARRANGEMENT GIVES

$$\underbrace{\langle a_k(\ell) | b_k(\ell) \rangle}_{=0} \underbrace{\langle u_i(i) | f(\mathbf{r}_i) | u_i(i) \rangle}_{\neq 0} = 0$$

$(N-1)!$  ways of arranging the  $e^-$  in the other  $N-1$  matched orbitals and  
there are  $N$  identical terms (in which the  $e^-$  is in the privileged location) in  
the sum over  $i$

$$\langle \psi_A | \mathbf{F} | \psi_B \rangle = (N!)^{-1} (N-1)! N \langle a_k | \mathbf{f} | b_k \rangle$$

## 5.73 Lecture #31

31 - 4

If the order of spin-orbitals in  $\psi_A$  or  $\psi_B$  must be arranged away from the standard order in order to match the positions of  $a_k$  and  $b_k$ , then we get an additional factor of  $(-1)^p$  where  $p$  is the number of binary permutations

$$\langle \psi_A | \mathbf{F} | \psi_B \rangle = (-1)^p \langle a_k | \mathbf{f} | b_k \rangle$$

for difference of one spin-orbital

i.e.  $A = \|12\ 5\ 7\|$

$$B = \|12\ 3\ 5\| = -\|12\ 5\ 3\|$$

$$\langle \psi_A | \mathbf{F} | \psi_B \rangle = -\langle 7 | \mathbf{F} | 3 \rangle$$

2.  $\psi_A = \psi_B$  Differ by zero spin-orbitals

$$\langle \psi_A | \mathbf{F} | \psi_B \rangle = (N!)^{-1} \sum_{i, \wp} \left[ \langle \mathbf{P}_i a_i(i) | \mathbf{f}(\mathbf{r}_i) | \mathbf{P}_i a_i(i) \rangle \right]$$

all other factors are =1

$N!$  identical terms from sum over  $\wp$  [again  $(N-1)!N$ ]

$$\langle \psi_A | \mathbf{F} | \psi_B \rangle = \sum_i \langle a_i | \mathbf{f}(\mathbf{r}_i) | a_i \rangle$$

- \* **Normalization** } comes out almost the same as naive expectation WITHOUT need for antisymmetrization!
- \*  $1 - e^-$  **Operator  $\mathbf{F}$**

Examples of  $f^3$ :  $\psi = \|3\alpha 1\alpha - 2\alpha\|$

$$\langle \mathbf{L}_z \rangle = \hbar(3 + 1 - 2)$$

$$\langle \mathbf{L}_z \mathbf{S}_z \rangle = \hbar^2 \left( \frac{3}{2} + \frac{1}{2} - 1 \right)$$

$$\mathbf{J}_+ \|3\alpha 1\alpha - 2\alpha\| = \mathbf{L}_+ \|3\alpha 1\alpha - 2\alpha\| + \mathbf{S}_+ \|3\alpha 1\alpha - 2\alpha\|$$

$$= \hbar [0 + 10^{1/2} \|3\alpha 2\alpha - 2\alpha\| + 10^{1/2} \|3\alpha 1\alpha - 1\alpha\| + 0 + 0 + 0]$$

now  $\mathbf{G}(i, j)$

C.  $G(i,j)$  : 4 cases

1. differ by more than 2 spin-orbitals: Matrix Element  $\rightarrow 0$
2. differ by 2 spin-orbitals: one pair of nonzero matrix elements
3. differ by 1 spin-orbital: sum over pairs of nonzero matrix elements
4. expectation value : differ by 0 spin-orbitals: double sum over pairs of matrix elements

1. is obvious — only way to make up for orbital mismatch is to hide the mismatched orbitals in  $\langle |g(i,j)| \rangle$  (rather than in an overlap integral). But one can only hide 2-mis-matched pairs in, e.g.

$$\langle a_i a_j | g(i, j) | b_i b_j \rangle$$

$$\langle \psi_A | \mathbf{G}(i, j) | \psi_B \rangle = 0 \quad \text{if } \psi_A, \psi_B \text{ differ by more than 2 pairs of spin-orbitals}$$

2. differ by two pairs of spin-orbitals

$$\psi_A = \| u_1(1) \dots a_1(i) \dots a_2(j) \dots u_N(N) \|$$

$$\psi_B = (-1)^p \| u_1(1) \dots b_1(i) \dots b_2(j) \dots u_N(N) \|$$

permutations needed to put  $b_1$  and  $b_2$  in the  $i$  and  $j$  positions

$$\langle \psi_A | \mathbf{G} | \psi_B \rangle = (N!)^{-1} \sum_{i>j} \sum_{\boldsymbol{\rho}, \boldsymbol{\rho}'} (-1)^{p+p'} [\text{orthogonality integrals}] \times$$

$$[\langle \mathbf{P}_i a_1(i) | \langle \mathbf{P}_j a_2(j) | g(i, j) | \mathbf{P}'_i b_1(i) \rangle | \mathbf{P}'_j b_2(j) \rangle]$$

\* are  $(N - 2)!$  ways of permuting the  $N - 2$  matched  $u_k$  functions that are not filled with  $e^-$   $i$  and  $j$ . Moreover these permutations must involve  $\mathbf{P}_k = \mathbf{P}'_k$  (all  $k \neq i, j$ ).

\* also  $N(N - 1)$  identical terms in sum over  $i > j$

# 5.73 Lecture #31

Thus there are  $(N-2)!(N-1)N = N!$  identical terms in  $\sum_{i>j} \sum_{\wp, \wp'}$  sums.

But there are still two possibilities:

1.  $\wp = \wp' \therefore p = p'$  and  $P_i = P'_i, P_j = P'_j$
2.  $\wp$  same as  $\wp'$  except for  $i, j$  pair where

THIS MEANS WE PUT THE  $j$ -th  $e^-$  in  $P'_j$  where WE PUT THE  $i$ -th  $e^-$  in  $P_i$

$$\left. \begin{matrix} P_i = P'_j \\ P_j = P'_i \end{matrix} \right\} (-1)^{p+p'} = -1$$

the 2  $\wp$ 's differ by one binary permutation

THUS:  $\langle \psi_A | G | \psi_B \rangle = \pm [ \langle a_1(1)a_2(2) | g(1,2) | b_1(1)b_2(2) \rangle - \langle a_1(1)a_2(2) | g(1,2) | b_2(1)b_1(2) \rangle ]$

For  $\psi_A, \psi_B$  different by 2 spin-orbitals

# of permutations needed to make  $\psi_B$  match  $\psi_A$   
 — no sign ambiguity if standard order is initially specified

3.  $\psi_A, \psi_B$  differ by only one pair of spin-orbitals

You work this out

$$\langle \psi_A | G | \psi_B \rangle = \pm \sum_n [ \langle \overbrace{a(1)u_n(2)}^{(a,b \text{ matched})} | g(1,2) | \overbrace{b(1)u_n(2)}^{(a,b \text{ matched})} \rangle - \langle \overbrace{a(1)u_n(2)}^{(a \text{ matched with } u_n, u_n \text{ matched with } b)} | g(1,2) | \overbrace{u_n(1)b(2)}^{(a \text{ matched with } u_n, u_n \text{ matched with } b)} \rangle ]$$

not arbitrary

4. differ by zero spin-orbitals : expectation value

$$\langle \psi_A | G | \psi_A \rangle = \sum_{n>m} [ \langle u_n(1)u_m(2) | g(1,2) | u_n(1)u_m(2) \rangle - \langle u_n(1)u_m(2) | g(1,2) | u_m(1)u_n(2) \rangle ]$$

DIRECT  
 what we would expect without antisymmetrization

EXCHANGE  
 unexpected: consequence of antisymmetrization

$$\rho_n^{(1)} \mathbf{g}^{(1,2)} \rho_m^{(2)}$$

The ONLY real surprise that results from the antisymmetrization requirement for two-electron operators is one extra term (and some signs) that has no counterpart if antisymmetrization had been ignored.

## SUMMARY

- \* antisymmetrize  $\rightarrow$  Slater determinants
- \* matrix elements are hardly more complicated than those of simple spin-orbital products
  - signs due to permutation [Standard order]
  - extra terms in  $G(i,j)$

Do some examples for  $p^2$

1. What L,S terms belong to  $p^2$  (Lecture #32: method of crossing out microstates)
2. What is the correct linear combination of Slater determinants that corresponds to a specific L-S term in either the  $|JLSM_J\rangle$  or the  $|LM_LSM_S\rangle$  basis set
  - ladders plus orthogonality (Lecture #32)
  - $L^2$  and  $S^2$  matrices
  - 3-j coefficients
3.  $e^2/r_{ij} \rightarrow F^k(n\ell, n'\ell'), G^k(n\ell, n'\ell')$  Slater Condon parameters  
relative energies of L - S terms expressed in terms of  $F^k$  and  $G^k$ 's
4. Matrix elements of  $H^{SO}$ 
  - $\zeta$  (NLS)
  - $\zeta$  (NLS)  $\leftrightarrow \zeta_{n\ell}$
  - full  $H^{SO}$  in terms of  $\zeta_{n\ell}$

EXAMPLES:

Slater :  $p^2 \quad \left\| 1\alpha 1\beta \right\| \rightarrow {}^1D \quad M_L = 2, M_S = 0$

$$\begin{aligned} \langle \mathbf{L}_z \rangle &= \langle \left\| 1\alpha 1\beta \right\| \mathbf{L}_z \left\| 1\alpha 1\beta \right\rangle \\ &= \hbar [1 + 1] = 2\hbar \end{aligned}$$

$$\langle \mathbf{S}_z \rangle = \hbar \left[ \frac{1}{2} + \left( -\frac{1}{2} \right) \right] = 0\hbar$$

$\mathbf{L}_z^2$       tricky!  $\mathbf{L}_z^2 = \underbrace{\sum_i \ell_{z_i}^2}_{1-e^- \text{ operator}} + \underbrace{\sum_{i \neq j} \ell_{z_i} \ell_{z_j}}_{2-e^- \text{ operator}}$

Easier to do this by applying  $\mathbf{L}_z = \sum_i \ell_{z_i}$  twice

The only 2 terms in sum are 1,2 & 2,1

$$\begin{aligned} \langle \mathbf{L}_z^2 \rangle &= \hbar^2 [1^2 + 1^2] + \sum_{i \neq j} \left[ \langle 1\alpha 1\beta | \ell_{z_i} \ell_{z_j} | 1\alpha 1\beta \rangle - \langle 1\alpha 1\beta | \ell_{z_i} \ell_{z_j} | \beta 1\alpha \rangle \right] \\ &= 2\hbar^2 + \hbar^2 [1^2 + 1^2 - \underbrace{0}_{\text{from spin-mismatch}} - \underbrace{0}_{\text{from spin-mismatch}}] = 4\hbar^2 \text{ as expected} \end{aligned}$$

$$\langle \mathbf{S}_z^2 \rangle = \hbar^2 \left[ \frac{1}{4} + \frac{1}{4} \right] + \hbar^2 \left[ -\frac{1}{4} - \frac{1}{4} - 0 - 0 \right] = 0\hbar^2 \text{ as expected}$$

$$\mathbf{L}^2 - \mathbf{L}_z^2 = \mathbf{L}_x^2 + \mathbf{L}_y^2 = \frac{1}{2} (\mathbf{L}_+ \mathbf{L}_- + \mathbf{L}_- \mathbf{L}_+)$$

$$\mathbf{L}^2 = \frac{1}{2} (\mathbf{L}_+ \mathbf{L}_- + \mathbf{L}_- \mathbf{L}_+) + \mathbf{L}_z^2$$

can you show  $\langle \mathbf{L}^2 \rangle = \hbar^2 6$  for  $\left\| 1\alpha 1\beta \right\|$  of  $p^2$ ?



Patterns of Lowest-Lying States: “Aufbau” for adults!

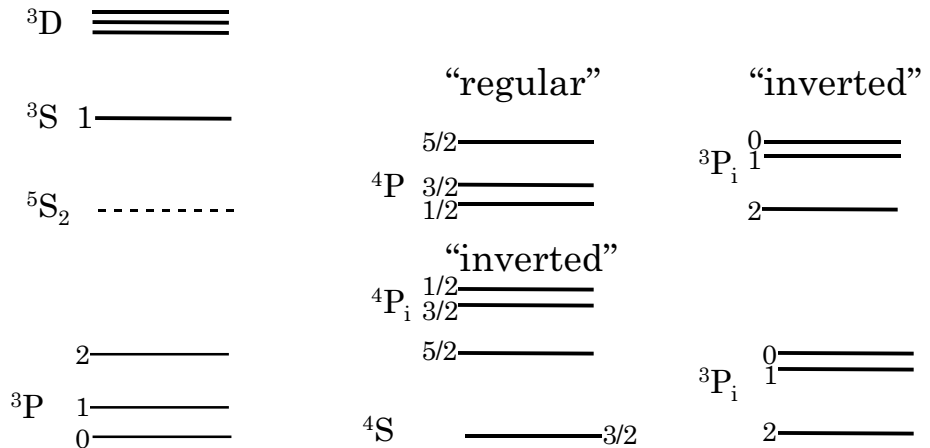
Atom	C	N	O
lowest config.	$1s^2 2s^2 2p^2$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^4$
L-S terms	$^1S, ^1D, ^3P$	$^4S, ^2P, ^2D$	$^1S, ^1D, ^3P$
Lowest Term	$^3P_0$	$^4S_{3/2}$	$^3P_2$

(regular) (no fine structure) (inverted)

	excitation	resultant configuration		
Transitions to lowest configurations $\Delta l = \pm 1$	$2p \leftarrow 2s$	$2s 2p^3$	$2s 2p^4$	$2s 2p^5$
	$3s \leftarrow 2p$	$2s^2 2p 3s$	$2s^2 2p^2 3s$	$2s^2 2p^3 3s$
	$3d \leftarrow 2p$	$2s^2 2p 3d$	$2s^2 2p^2 3d$	$2s^2 2p^3 3d$
[lowest L-S-J term of each configuration]	$^{5,3}S, ^{3,1}P, ^{3,1}D$	$^{2,4}P, ^2D, ^2S$	$^{2,4}P, ^2D, ^2S$	$^{1,3}P$
	$[^5S_2]$	$[^4P_{5/2}]$	$[^4P_{1/2}]$	$[^3P_2]$
	$^{1,3}P$	$^{2,4}P, ^2D, ^2S$	$^{2,4}F, ^2P, ^2D, ^2G, ^2S$	$^{5,3}S, ^{3,1}P, ^{3,1}D$
	$[^3P_0]$	$[^4P_{1/2}]$	$[^4F_{3/2}]$	$[^5S_2]$
	$^{1,3}F, ^{1,3}P$			$^{5,3}D, ^{3,1}F, ^{3,1}P, ^{1,3}G, ^{1,3}S$
	$[^3F_2]$			$[^5D_0]$

characteristic transition (2p ↔ 2s)

lowest L-S states of the two relevant configuration



$$\zeta_{2p}(C) < \zeta_{2p}(N) < \zeta_{2p}(O)$$