Matrix Elements of One-Electron, *F*(*i*), and Two-Electron, *G*(*i,j*), Operators

Last time: orbitals → configurations → <u>states</u> ("terms")
Fermions: Slater Determinants: Pauli Exclusion Principle
Compact Notation for Slater Determinant: $\|$main diagonal$\|$.

TODAY: 1. SLATER DETERMINANTAL MATRIX ELEMENTS

A. Normalization

B. $F(i)$: One-e$^-$ operator e.g. $\mathrm{H}^{SO}=\sum_i a(r_i)\boldsymbol{\ell}_i\cdot \mathrm{s}_i$

C. $G(i,j)$: Two-e$^-$ operator e.g. $\mathrm{H}^{\mathrm{e}}=\sum_{i>j} e^2/\mathrm{r}_{ij}$

Recall: specify a standard order of spin-orbitals (because determinant changes sign upon every binary permutation)

Goal: make the 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 pages 30-6, 7, 8

A. Normalization: $|\psi_N\rangle=(N!)^{-1/2}\sum_{\wp}(-1)^p\wp\left[|u_1(1)\rangle\ldots|u_N(N)\rangle\right]$ anti-symmetrized product of spin-orbitals

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

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

rearrange into products of one-e$^-$ overlap integrals:

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

- * $\{|u_i\rangle\}$ are orthonormal
- * $\langle u(i)|u(j)\rangle$ has no meaning because bra and ket must be associated with the SAME electron
- * only non-zero LEGAL terms in $\sum_{\wp\,\wp'}$ are those where EACH $\mathbf{P}_i=\mathbf{P}'_i$, otherwise get AT LEAST 2 MISMATCHED bra-kets

$$\underbrace{\langle u_i(k)|u_j(k)\rangle}_{=0}\ldots\underbrace{\langle u_j(\ell)|u_i(\ell)\rangle}_{=0}$$

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

Think of a one- or two-e$^-$ 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 $$\langle \psi_N | \psi_N \rangle = (N!)^{-1} \sum_{\wp} \wp \Big[\underbrace{\langle \mu_1(1) | \mu_1(1) \rangle}_{=1} \ldots \underbrace{\langle \mu_N(N) | \mu_N(N) \rangle}_{=1} \Big].$$

Each term in the sum over $\wp$ gives +1, but there are N possibilities for $\mathbf{P}_1$, N – 1 possibilities for $\mathbf{P}_2$, N_2 – 2 possibilities for $\mathbf{P}_3$ …

$$\therefore N! \text{ possibilities for sum over } \wp$$

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

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

B. Matrix elements of one-electron operators

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

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

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

$$\langle \psi_A | \mathbf{F} | \psi_B \rangle = (N!)^{-1} \sum_{i,\wp,\wp'} (-1)^{p+p'} \wp \big[\langle a_1(1) | \ldots \big] f(\mathbf{r}_i) \wp' \big[|b_1(1)\rangle \ldots \big]$$

$$= (N!)^{-1} \sum_{i,\wp,\wp'} (-1)^{p+p'} \big[\langle \mathbf{P}_1 a_1(1) | \mathbf{P}_1 b_1(1) \rangle \big]$$

$$\ldots \Big[\Big\langle \mathbf{P}_i a_i(i) \Big| f(\mathbf{r}_i) \Big| \mathbf{P}'_i b_i(i) \Big\rangle \Big] \ldots \big[\langle \mathbf{P}_N a_N(N) | \mathbf{P}'_N b_N(N) \rangle \big]$$

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^- operator.

1. 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 in the N-term product would be zero)

two cases remain:

2. $|\Psi_A\rangle$ and $|\Psi_B\rangle$ differ by one spin-orbital

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

use u_i to denote the in-common spin-orbitals
use a_k, $b_k \neq 0$ to denote unique spin-orbitals

For this choice, all N $\mathbf{P}_i$ factors of each $\wp$ must be identical to all N $\mathbf{P}'_i$ factors of $\wp'$

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

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 orbital pairs, and there are N identical terms (in which the e^- is in the privileged location) in the sum over *i*

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

If the order of spin-orbitals in Ψ_A or Ψ_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

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

for a difference of one spin-orbital

i.e.

$$A = \|1\,2\;5\;7\|$$

$$B = \|1\,2\,3\,5\| = -\|1\,2\,5\,3\|$$

$$\left\langle \psi_A \middle| \mathbf{F} \middle| \psi_B \right\rangle = -\left\langle 7 \middle| \mathbf{f} \middle| 3 \right\rangle$$

a many-e⁻ integral is reduced to a single spin-orbital integral

3. $\Psi_A = \Psi_B$ Differ by zero spin-orbitals

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

all other factors are =1

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

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

* Normalization
and
* 1-e^- Operator **F**

comes out almost the same as naive expectation WITHOUT need to deal with antisymmetrization!

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

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

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

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

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

now $\mathbf{G}(i,j)$: A two-electron operator

C. $\mathbf{G}(i,j)$: 4 cases

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

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

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

2. differ by two pairs of spin-orbitals

$$\psi_A = \left\| u_1(1) \ldots a_1(i) \ldots a_2(j) \ldots u_N(N) \right\|$$

$$\psi_B = (-1)^{p} \left\| u_1(1) \ldots b_1(i) \ldots b_2(j) \ldots u_N(N) \right\|$$

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

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

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

* there 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 $\mathbf{P}_k = \mathbf{P}'_k$ (for all $k \neq i,j$).

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

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

But there still remain two possibilities:

1. $\wp = \wp' \quad \therefore p = p'$ and $\mathbf{P}_i = \mathbf{P}'_i,\ \mathbf{P}_j = \mathbf{P}'_j$
2. $\wp$ same as $\wp'$ except for i, j pair where

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

$$\left.\begin{matrix}\mathbf{P}_i = \mathbf{P}'_j \\ \mathbf{P}_j = \mathbf{P}'_i\end{matrix}\right\rangle \underbrace{(-1)^{p+p'}}_{} = -1$$

The 2 $\wp$' s must differ by exactly one binary permutation

$$\text{THUS: } \left\langle \psi_A \middle| \mathbf{G} \middle| \psi_B \right\rangle = \pm\left[\left\langle a_1(1)a_2(2)\middle|g(1,2)\middle|b_1(1)b_2(2)\right\rangle - \left\langle a_1(1)a_2(2)\middle|g(1,2)\middle|b_2(1)b_1(2)\right\rangle\right]$$

For ψ_A, ψ_B different by 2 spin-orbitals:

\# of permutations needed to make ψ_B match ψ_A — no sign ambiguity if standard order is initially specified

3. ψ_A, ψ_B differ by only one pair of spin-orbitals

You work this out

(a, b matched)

[(a matched with u_n), u_n matched with b]

$$\left\langle \psi_A \middle| \mathbf{G} \middle| \psi_B \right\rangle = \pm \sum_{\substack{n \\ n\neq 1,2}} \left[\left\langle a(1)u_n(2)\middle|g(1,2)\middle|b(1)u_n(2)\right\rangle - \left\langle a(1)u_n(2)\middle|g(1,2)\middle|u_n(1)b(2)\right\rangle\right]$$

(a with u_n)

not arbitrary

4. differ by zero spin-orbitals : expectation value of **G**

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

"DIRECT"	"EXCHANGE"
what we would expect without antisymmetrization	unexpected: consequence of antisymmetrization

The ONLY real surprise that results from the anti-symmetrization requirement for two-electron operators is the presence of one additional term and some signs that would have no counterpart if anti-symmetrization had been ignored.

SUMMARY

* antisymmetrize → Slater determinants

* matrix elements are only slightly more complicated than those of a simple product of spin-orbitals

- signs due to permutation [away from Standard Order]
- extra terms in matrix elements of $\mathbf{G}(i,j)$

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?

Methods:

- ladders plus orthogonality (Lecture #32)
- $\mathbf{L}^2$ and $\mathbf{S}^2$ matrices (Lecture #33)
- 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. (Lecture #34)

4. Matrix elements of $\mathbf{H}^{SO}$ (Lecture #35)

- $\zeta(NLS)$: coupling constant for an N–L–S state
- $\zeta(NLS) \leftrightarrow \zeta_{n\ell}$: relation of $\zeta(NLS)$ to orbital integrals
- full $\mathbf{H}^{SO}$ in terms of $\zeta_{n\ell}$
- periodic table explains the $\zeta_{n\ell}$, but the $\zeta(NLS)$ do not directly display periodicity. WHAT WE WANT IS ENCODED IN WHAT WE CAN OBSERVE

EXAMPLES:

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

$$\langle \mathbf{L}_z \rangle = \langle \left\|1\alpha 1\beta\right\| \mathbf{L}_z \left\|1\alpha 1\beta\right\| \rangle$$

$$= \hbar[1+1] = 2\hbar$$

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

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

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

$$\langle \mathbf{L}_z^2 \rangle = \hbar^2\left[\ell_{z_1}^2 + \ell_{z_2}^2\right] + \sum_{i \neq j} \left[\langle 1\alpha 1\beta | \ell_{z_i} \ell_{z_j} | 1\alpha 1\beta \rangle - \langle 1\alpha 1\beta | \ell_{z_i} \ell_{z_j} | 1\beta 1\alpha \rangle\right]$$

from spin-mismatch

$$= 2\hbar^2 + \hbar^2\left[1^2 + 1^2 - 0 - 0 = 4\hbar^2 \text{ as expected}\right]$$

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

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

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

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

Patterns of Lowest-Lying States: "Aufbau" for adults!

Atom	C	N	O
lowest config.	$1s^22s^22p^2$	$1s^22s^22p^3$	$1s^22s^22p^4$
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")

	C	**N**	**O**
excitation 2p ← 2s	$2s2p^3$ $^{5,3}S$, $^{3,1}P$, $^{3,1}D$ $[^5S_2]$	$2s2p^4$ $^{4,2}P$, ^2D, ^2S $[^4P_{5/2}]$	$2s2p^5$ $^{3,1}P$ $[^3P_2]$
3s ← 2p	$2s^22p^2\,3s$ $^{3,1}P$ $[^3P_0]$	$2s^22p^2\,3s$ $^{4,2}P$, ^2D, ^2S $[^4P_{1/2}]$	$2s^22p^3\,3s$ ^5S, $^3(D,P,S)$ $[^5S_2]$
3d ← 2p	$2s^22p\,3d$ $^{3,1}(F,D,P)$ $[^3F_2]$	$2s^22p^2\,3d$ $^2(G,F,D,D,D,P,P,S)$, $^4(F,D,P)$ $[^4P_{1/5}]$	$2s^22p^3\,3d$ ^5D, $^3(GFFDDDPPS)$, $^1(GFFDDPPS)$ $[^5D_0]$

Energy Levels of Lowest and First Excited Configurations

		C		N		O
	$^1P_1$	119878 cm^{-1}				
	$^3S_1$	105800				
	$^1D_2$	97878				
	IP($^2P_{1/2}$)	90878				
	$^3P_{2,1,0}$	75256			$^1P_1$	189837
	$^3D_3$	64088	IP($^3P_0$)	117345	$^3P_0$	126266
	$^3D_2$	64093	$^4P_{1/2}$	88173	$^3P_1$	126340
	$^3D_1$	64092	$^4P_{3/2}$	88153	$^3P_2$	126266
	$^5S_2$	33735	$^4P_{5/2}$	88110	IP($^4S_{3/2}$)	109827
	$^1S_0$	21648			$^1S_0$	33794
	$^2D_2$	10194	$^2P_{3/2,1/2}$	28840	$^1D_2$	15868
Lowest Configuration	$^3P_2$	44	$^2D_{3/2}$	19231	$^2P_0$	226
	$^3P_1$	16	$^2D_{5/2}$	19223	$^2P_1$	158
	$^3P_0$	0	$^4S_{3/2}$	0	$^2P_2$	0

How does one begin to assign an atomic spectrum? You need predictions of the *L-S-J* symmetry of the electronic ground state (because all absorption spectra will originate from this ground state) and the symmetries of the upper states of the lowest energy allowed transitions to the expected lowest excited electronic configurations. This should be simple, right?

The energy levels for C I, N I, and O I (the I denotes neutral, II denotes singly charged, III...) are tabulated in Atomic Energy Levels as Derived from the Analysis of Optical Spectra (NSRDS-NBS 35, volume 1) are available on-line. There are an enormous number of assigned energy levels listed in the tables. One thing should be immediately clear: there are no obvious patterns. The energy levels that belong to the same electronic configuration are often widely spaced. *Where is the Periodic Table in all of this apparent complexity?*

The spin-orbit constants, z_{2p}, for the 2p orbital in C, N, and O are: 29.0, 53.7, and 151 cm-1 respectively (Lefebvre-Brion and Field, The Spectra and Dynamics of Diatomic Molecules, page 316, Elsevier, 2004). These spin-orbit constants clearly exhibit the qualitative effects implicit in the Periodic Table.

Where is the **periodic table** in all of this? The electronic spectra and the energy level diagrams for C, N, and O atoms are complicated and, most importantly, there are no apparent relationships among them. You need a *magic decoder* to assign the spectra and another *magic decoder* to discover how the spectra relate to **periodicity**. The intra-configurational splittings due to matrix elements of the $1/r_{ij}$ inter-electronic repulsion term are enormous (in some cases comparable to the ionization energy) and do not follow any obvious pattern. The matrix elements of $1/r_{ij}$ are expressed in terms of Slater-Condon parameters (F_k and G_k). The two-electron F_k and G_k terms, one-electron orbital energies, and one-electron spin-orbit constants all exhibit recognizable and interpretable periodicity. To me, this is staggeringly beautiful and a large part of the reason I chose electronic spectroscopy as the core of my career research.

5.73 Quantum Mechanics I
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