

Matrix Elements of Many-Electron Wavefunctions

Last time:

$$\nu = \left[-\frac{\mathfrak{R}}{E_{n,\ell}} \right]^{1/2} \quad \text{noninteger principal quantum number}$$

$$\left. \begin{array}{l} f_\ell(\nu, r) \\ g_\ell(\nu, r) \end{array} \right\} \quad \text{solutions to Schröd. Eq. outside sphere of radius } r_0$$

need both f and g to satisfy boundary condition for $E < 0$ as $r \rightarrow \infty$

$$\nu = n - \mu_\ell$$

$\pi\mu_\ell$ is phase shift of $f_\ell(\nu, r)$

infinite set of integer-spaced ν -values that satisfy $r \rightarrow \infty$ boundary condition

Wave emerges from core with ν -independent phase. Core transforms wave with correct $r \rightarrow 0$ limiting behavior into one that exits imaginary sphere of radius r_0 , which contains the core region, with $\pi\mu_\ell$ phase shift.

Core sampled by set of different ℓ 's.

Today:

Wavefunctions and Energy States of many-electron atoms

1. orbitals \rightarrow configurations \rightarrow L - S states
2. electrons are Fermions \rightarrow ψ must be “**antisymmetrized**”: KEY PROBLEM
3. Slater determinants are antisymmetric wrt all e_i^-, e_j^- permutations
 - A. Normalization
 - B. Matrix Elements of one - e^- Operators: e.g. $\mathbf{H}^{SO} = \sum_i a(r_i) \boldsymbol{\ell}_i \cdot \mathbf{s}_i$
 - C. Matrix Elements of two - e^- Operators: e.g. $\mathbf{H}^e = \sum_{i>j} e^2 / \mathbf{r}_{ij}$
(a very bad “perturbation”)
4. \mathbf{H}^{eff} in terms of $\varepsilon_{n\ell}$, $\underbrace{F^k, G^k}_{\substack{\text{Slater-Condon} \\ 1/r_{ij}}}$, $\zeta_{n\ell}$ parameters

orbital energy	$\underbrace{F^k, G^k}_{\substack{\text{Slater-Condon} \\ 1/r_{ij}}}$	spin- orbit
-------------------	---	----------------

next few
lectures

Page 31-9 is an example of what we will be able to do.

* Interpretable trends: Periodic Table

* Atomic energy levels: mysterious code — no atom-to-atom relationships evident without magic decoder ring.

Many-electron \mathbf{H}

$$\mathbf{H} = \underbrace{\sum_{i=1}^N \mathbf{h}(i)}_{\mathbf{H}^{(0)}} + \underbrace{\sum_{i>j=1}^N \frac{e^2}{r_{ij}} + \sum_i \alpha(r_i) \ell_i \cdot \mathbf{s}_i}_{\mathbf{H}^{(1)}}$$

sum of hydrogenic

$$1\text{-}e^- \text{ terms: } -\frac{Z^2 \mathcal{R}}{n^2} = -\epsilon_n \quad (\text{unshielded orbital energies})$$

How do we set up matrix representation of this \mathbf{H} ? $\mathbf{H}^{(0)}$ defines basis set (complete, orthonormal, ...)

$$\mathbf{H}^{(0)} = \sum_{i=1}^N \mathbf{h}(i) \leftrightarrow |\psi\rangle = \prod_{i=1}^N \left[\begin{array}{c} \text{spatial} \\ \text{part} \end{array} \left| \phi_i(r_i) \right\rangle \left| \begin{array}{c} \text{spin} \\ \text{part} \end{array} sm_s(i) \right\rangle \right]$$

“spin-orbital”

the $\phi_i(r_i)$'s could be
hydrogenic or
shielded-core
Rydberg-like orbitals.

$$[\mathbf{h}(1) + \mathbf{h}(2)]\phi(1)\phi(2) = [\mathbf{h}(1)\phi(1)]\phi(2) + [\mathbf{h}(2)\phi(2)]\phi(1)$$

└ a constant with respect to $\mathbf{h}(1)$.

 \mathbf{H} as sum, \mathbf{E} as sum, ψ as productElectronic Configuration: list of orbital occupanciese.g. C $1s^2 2s^2 2p^2$ six e^-

not sufficient to specify state of system

several L, S terms arise from this configuration: e.g. $p^2 \rightarrow {}^1D, {}^3P, {}^1S$

$$\vec{L} \equiv \sum_i \vec{\ell}_i \quad \vec{S} \equiv \sum_i \vec{s}_i$$

we know that L^2, L_z, S^2, S_z commute with $\mathbf{h}(i) + \frac{e^2}{r_{ij}}$ so we can use these to block diagonalize \mathbf{H} .

Note that although $\vec{\ell}_i$ does not commute with e^2/r_{ij} , this is not a problem for \mathbf{s}_i^2 and \mathbf{s}_{iz} because $\mathbf{h}(i)$ and \mathbf{r}_{ij} do not involve spin. \mathbf{r}_{ij} destroys ℓ_i but not \mathbf{L} !

5.73 Lecture #30

30 - 3

How do we get eigenstates of L^2, L_z, S^2, S_z ?

- either:
- I. Method of M_L, M_S boxes
Advanced Inorganic
Which L-S terms exist, **not** the specific linear combinations of spin-orbital products that correspond to these terms.
 - II. Angular momentum coupling techniques
3-j
ladders plus orthogonality
projection operators

We will return to this problem and approach it both ways.

One rigorous symmetry must be imposed:

Pauli Exclusion Principle: electrons are Fermions and therefore any acceptable wavefunction must be antisymmetric with respect to permutation of ANY pair of e^-

e.g. $|1, 2\rangle = \overbrace{|u_1(1)\rangle|u_2(2)\rangle}^{\text{electrons}}$
orbitals

$$\mathbf{P}_{12}|1, 2\rangle = |u_1(2)\rangle|u_2(1)\rangle \equiv |2, 1\rangle$$

$$e^- \text{ are indistinguishable, } \therefore [\mathbf{H}, \mathbf{P}_{ij}] = 0$$

\therefore all ψ 's must belong to + or - eigenvalue of \mathbf{P}_{ij} (note that $\mathbf{P}_{ij}^2 = \mathbf{I}$)

- + Boson (integer spin)
- Fermion (1/2 integer spin)

$$\psi_{\pm} = 2^{-1/2} [|1, 2\rangle \pm |2, 1\rangle]$$

$$\mathbf{P}_{12}\psi = 2^{-1/2} [|2, 1\rangle \pm |1, 2\rangle] = \pm\psi_{\pm}$$

ψ_+ bosons
 ψ_- fermions

5.73 Lecture #30

30 - 4

generalize to 3 e⁻? 3! combinations needed! Horrible

ψ 's have N! terms (each a product of N spin-orbitals)

matrix elements have (N!)² additive terms!

TRICK! Slater Determinants

$$\begin{array}{c} \overbrace{\hspace{1.5cm}}^{e^-} \\ \left| \begin{array}{cc} u_1(1) & u_2(1) \\ u_1(2) & u_2(2) \end{array} \right| = u_1(1)u_2(2) - u_1(2)u_2(1) \\ \underbrace{\hspace{1.5cm}}_{\text{orbital}} \qquad \text{row is label for } e^- \\ \qquad \qquad \qquad \text{column is label for spin-orbital} \end{array}$$

you show that 3 × 3 Slater determinant gives 6 additive product terms

Determinants N × N

- * N! terms in expansion of determinant
- * determinant changes sign upon permutation of ANY two rows [e⁻'s] or columns [spin-orbitals]
- * determinant is zero if any two rows or columns are identical.
- * determinant may be uniquely specified by main diagonal

**MUST SPECIFY IN ADVANCE A STANDARD ORDER
IN WHICH THE SPIN-ORBITALS ARE TO BE LISTED
ALONG MAIN DIAGONAL**

e.g. $s\alpha, s\beta, p1\alpha, p1\beta, p0\alpha, p0\beta, p-1\alpha, p-1\beta, \dots$

[or for p^N, suppress p in notation: $1\alpha1\beta0\alpha \oslash M_L = 2, M_S = 1/2$]

Need a fancy notation to demonstrate how Slater determinants are to be manipulated in evaluating matrix elements. This notation is to be forgotten as soon as it has served its immediate purpose here.

$$|\psi_N\rangle = (N!)^{-1/2} \sum_{\wp} (-1)^p \wp \left[|u_1(1)\rangle \dots |u_N(N)\rangle \right]$$

of binary permutations \swarrow
N! different \wp 's \swarrow

\wp is ONE prescription for rearranging the orbitals from the initially specified order

\wp is product of several P_{ij} 's or, more useful for proving theorems, a product of N factors P_i which tell whether the i-th electron is to be left in the i-th spin-orbital or transferred to some unspecified spin-orbital

$$\wp \left[|u_1(1)\rangle \dots |u_N(N)\rangle \right] = \prod_{i=1}^N |P_i u_i(i)\rangle$$

A. Normalization

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

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

Now rearrange into products of one - e^- overlap integrals,

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

$|u_i\rangle$ are orthonormal

$\langle u(i) | u(j) \rangle$ has no meaning because bra and ket must be associated with same e^-

The only nonzero legal terms in $\sum_{\wp, \wp'}$ are those where EACH $P_i = P'_i$

otherwise there will be AT LEAST 2 mis-matched bra - kets

$$\begin{aligned} \langle u_i(k) | u_j(k) \rangle \dots \langle u_j(\ell) | u_i(\ell) \rangle \\ = 0 \qquad \qquad \qquad = 0 \end{aligned}$$

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

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

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

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

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

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

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

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⁻ operator.

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 #30

30 - 8

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

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

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 : $\psi = \|3\alpha 1\alpha - 2\alpha\|$

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

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

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

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

next time $\mathbf{G}(i,j)$