Matrix Elements of Many-Electron Wavefunctions

Last time:

$$v=\left[-\frac{\Re}{E_{n,\ell}}\right]^{1/2}$$ non-integer principal quantum number ($E_{\infty,\ell}=0$)

$$\left.\begin{matrix} f_\ell(v,r) \\ g_\ell(v,r \end{matrix}\right\}$$ two linearly independent solutions to Schrödinger Equation are valid outside sphere of radius r_0

Need <u>both</u> *f* and *g* to satisfy boundary condition for E → 0 as r → ∞

$$\nu = n-\mu_\ell \left(\text{non-integer } \nu\right)$$
$$\pi\mu_\ell \text{ is phase shift of } f_\ell\left(\nu,r\right)$$

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

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

Core is sampled by a set of different ℓ values.

Today:

Wavefunctions and Energy States of many-electron atoms: a magic decoder

1. (spin) orbitals → configurations → L-S states
2. electrons are Fermions → ψ must be "antisymmetrized": KEY PROBLEM
3. Slater determinants are antisymmetric with respect to *all* e_i^-, e_j^- permutations
   - A. Normalization
   - B. Matrix Elements of one-e⁻ Operators: e.g. $\mathbf{H}^{\text{SO}}=\sum_i a\left(r_i\right)\ell_i\cdot\mathbf{s}_i$
   - C. Matrix Elements of two-e⁻ Operators: e.g. $\mathbf{H}^e=\sum_{i>j} e^2/\mathbf{r}_{ij}$ (a very strong "perturbation")

next few lectures

4. H^{eff} in terms of $\underset{\text{orbital energy}}{\varepsilon_{n\ell}}$, $\underbrace{F^k,G^k}_{\substack{\text{Slater-Condon}\\ 1/r_{ij}}}$, $\underset{\text{spin-orbit}}{\zeta_{n\ell}}$ parameters

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 **H**

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

sum of hydrogenic

$1-e^-$ terms: $-\frac{Z^2\Re}{n^2} = -\varepsilon_n$ (unshielded hydrogenic orbital energies)

How do we set up a matrix representation of this **H**?

take as much as possible out of $\langle \mathbf{H}^{(1)} \rangle$

$\mathbf{H}^{(0)}$ defines the basis set (complete, orthonormal, ...)

$$\mathbf{H}^{(0)} = \sum_{i=1}^{N} \mathbf{h}(i) \leftrightarrow |\psi\rangle = \prod_{i=1}^{N} \Big[\overset{\text{spatial part}}{|\phi_i(r_i)\rangle} \overset{\text{spin part}}{|sm_s(i)\rangle} \Big]$$

"spin-orbital"

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

For two e⁻:

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

a constant with respect to **h**(1).

H as sum, E as sum, but get Ψ as product

Electronic Configuration: list of orbital occupancies

e.g. C $1s^22s^22p^2$ six e⁻

This is not sufficient to specify the state of a system

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

$\vec{L} \equiv \sum_i \vec{\ell}_i$ $\vec{S} \equiv \sum_i \vec{s}_i$ $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$

We know that $\mathbf{L}^2, \mathbf{L}_z, \mathbf{S}^2, \mathbf{S}_z$ commute with $\mathbf{h}(i) + \frac{e^2}{r_{ij}}$

So we can use thse to bock diagonalize **H**

$$|r_{12}| = \Big[|r_1|^2 + |r_2|^2 - \underbrace{2r_1 \bullet r_2}_{} \Big]^{1/2}$$

vector with respect to ℓ_1 and ℓ_2
scalar with respect to L

Note that although ℓ_i does not commute with e^2/r_{ij}, this is not a problem for s_i^2 and s_{iz} because $\mathbf{h}(i)$ and r_{ij} do not involve spin.

r_{ij} destroys ℓ_i but does not destroy L!

How do we get eigenstates of $\mathbf{L}^2$, $\mathbf{L}_z$, $\mathbf{S}^2$, $\mathbf{S}_z$

either: I. Method of M_L, M_S boxes
Advanced Inorganic Chemistry Course
Which L–S "terms" exist, but **not** the specific linear combinations of spin-orbital products that correspond to these terms.

II. Angular momentum coupling techniques:
3-j coefficients
ladders plus orthogonality
projection operators

We will return to this problem and approach it in all 3 angular momentum coupling 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⁻

electrons

$$\text{e.g.}\quad \left|1,2\right\rangle = \left|\mu_1(1)\right\rangle\left|\mu_2(2)\right\rangle$$

orbitals

$$\mathbf{P}_{12}\left|1,2\right\rangle = \left|\mu_1(2)\right\rangle\left|\mu_2(1)\right\rangle \equiv \left|2,1\right\rangle$$

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

$\therefore$ 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)

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

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

ψ_+ bosons
top sign

ψ_- fermions
bottom sign

generalize to 3 e$^-$? 3! combinations needed! Horrible!

- * ψ’s have N! terms (each is a product of N spin-orbitals)
- * matrix elements have $(N!)^2$ additive terms! Even more horrible!

TRICK! Slater Determinants

e$^-$

$$\begin{vmatrix} \mu_1(1) & \mu_2(1) \\ \mu_1(2) & \mu_2(2) \end{vmatrix} = \mu_1(1)\mu_2(2) - \mu_1(2)\mu_2(1)$$

orbital

row is label for e$^-$
column is label for spin-orbital

$$\begin{vmatrix} u_1(1) & \cdots & u_n(1) \\ \vdots & \vdots & \vdots \\ u_1(n) & & \end{vmatrix}$$

You show that a 3 × 3 Slater determinant gives 6 additive product terms

Determinants are of N × N dimension

- * N! additive 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 its main diagonal

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

e.g. $s\alpha,\ s\beta,\ p1\alpha,\ p1\beta,\ p0\alpha,\ p0\beta,\ p\text{-}1\alpha,\ p\text{-}1\beta,\ \ldots$

[or for p^N, suppress p in notation: $1\alpha 1\beta 0\alpha \rightarrow M_L = 2,\ M_S = 1/2$]

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

$\boxed{\text{\# of binary permutations away from “standard order”}}$

$$\left|\psi_N\right\rangle = (N!)^{-1/2}\sum_{\wp}(-1)^{p}\wp\Big[\left|\mu_1(1)\right\rangle\ldots\left|\mu_N(N)\right\rangle\Big]$$

$\boxed{\text{N! different }\wp\text{'s}}$

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

$\wp$ is product of several $\mathbf{P}_{\mathrm{ij}}$' s or, more useful for proving theorems, a product of N factors $\mathbf{P}_{\mathrm{i}}$ which specify whether the i$^{\mathrm{th}}$ electron is to be left in the i$^{\mathrm{th}}$ spin-orbital or transferred to some unspecified spin-orbital

$$\wp\Big[\left|\mu_1(1)\right\rangle\ldots\left|\mu_N(N)\right\rangle\Big]\prod_{i=1}^{N}\left|P_i\mu_i(i)\right\rangle$$

A. Normalization

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

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

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

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

The $\left|u_i\right\rangle$ are orthonormal.

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

The only non-zero legal terms in $\sum\limits_{\wp\,\wp'}$ are those where EACH $\mathbf{P}_i = \mathbf{P}'_i$

otherwise there will be at least 2 mis-matched bra-kets

$$\underset{=0}{\left\langle u_i(k)\middle|u_j(k)\right\rangle}\ldots\underset{=0}{\left\langle u_j(\ell)\middle|u_i(\ell)\right\rangle}$$

(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

$$\langle \Psi_N | \Psi_N \rangle = (N!)^{-1} \sum_{\wp} \wp \left[\langle \mu_1(1) | \underset{=1}{\mu_1(1)} \rangle \ldots \langle \mu_n(N) | \underset{=1}{\mu_n(N)} \rangle \right]$$

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

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

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

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

B. Matrix elements of one-electron operators

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

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

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

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

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

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

special term because indices match for e^- in both orbitals and the operator.

There is a 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.

Consider the 3 possibilities for 1-e$^-$ operators: Δso = 0, =1 or > 1.

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

two cases remain:

1. differ by one spin-orbital

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

Use u_i to denote common spin-orbitals
Use a_k, b_k to denote unique spin-orbitals

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

There is an 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

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

(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*

$$\langle \psi_A | \mathbf{F} | \psi_B \rangle = (\underset{\substack{\uparrow \\ \text{from the } (N!)^{-1/2} \text{ normalization factor for each } |\psi\rangle}}{N}!)^{-1} (N-1)! N \langle a_k | \mathbf{f} | b_k \rangle$$

If the order of spin-orbitals in ψ_A or ψ_B <u>must be arranged</u> 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 required number of binary permutations

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

for a difference of one spin-orbital

i.e.

$$A = \left\| 12\ 5\ 7 \right\|$$

$$B = \left\| 12\,3\,5 \right\| = -\left\| 12\,5\,3 \right\|$$

(one binary permutation is required)

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

2. $\Psi_A = \Psi_B$ <u>Differ by zero spin-orbitals</u>

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

all other factors are =1

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

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

* Normalization

and

* $1\text{-}e^-$ Operator **F**

} comes out <u>almost</u> the same as naive expectation WITHOUT need for antisymmetrization!

what is new? only the factor of $(-1)^P$ for re-ordering $|\psi_B\rangle$ to match order in $|\psi_A\rangle$

Examples of f^3:

$$\psi = \left\| 3\alpha 1\alpha -2\alpha \right\| \qquad (\lambda = 3, \lambda = 1, \lambda = -2)$$

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

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

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

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

YOU VERIFY!

next time **G***(i,j)*, a 2-electron operator.

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