Lecture 23 Supplement: Slater De- terminantal Matrix Elements

Slater Determinantal Matrix Elements of Zero–, One–, and Two–Electron Operators

An $N \times N$ determinant expands into $N!$ additive terms. A matrix element in a Slater determinantal basis set consists of the sum of $(N!)^2$ additive terms. If anti–symmetrization were not required for an N–fermion system, a matrix element would consist of a single term. It turns out that the situation for matrix elements of determinantal basis states is only slightly more complicated than the single term expected for a non–anti-symmetrized basis state. The following notes explain this surprising reduction in the labor associated with evaluation of determinantal matrix elements.

It is necessary to consider three types of matrix elements, which involve zero-, one-, and two-electron operators. A zero-electron operator is a constant, usually just an overlap integral. A one-electron operator could involve an angular momentum z-component operator

$$\sum_{i=1}^{N} \hat{s}_{z,i}$$

a spin-orbit operator

$$\sum_{i=1}^{N} a(r_i)\ell_i \cdot s_i = \sum_{i=1}^{N} a(r_i) \left[\ell_{z,i}s_{z,i} + \frac{1}{2}(\ell_{+,i}\, s_{-,i} + \ell_{-,i}s_{+,i}) \right]$$

or a transition moment operator

$$e\sum_{i} \vec{r}_i.$$

A two-electron operator could be the inter-electron repulsion operator

$$\sum_{i>i=1}^{N} \frac{e^2}{r_{ij}}.$$

Let's deal with each of these operators in sequence.

(1) Zero–electron operators

The selection rule for non-zero matrix elements of such operators is $\Delta so = 0$, where *so* is an abbreviation for spin-orbital, e.g. $1s\alpha$. It is convenient to label the spin-orbitals in some agreed-upon standard order $(1, 2, 3, \ldots, M)$ [where $M \gg N$ because there are more possibly-relevant spin-orbitals (M) than the number needed for a particular N–electron state (N)]. The N–electron matrix element of operator $\hat{c}$ (a constant) is

$$c \langle \psi_N | \psi_N \rangle = \int \sum_{\{n_i\}} 1(n_1)2(n_2)\ldots N(n_N)$$

$$c \langle \psi_N | \psi_N \rangle = \int c \left[\sum_{\{n_i\}} 1(n_1)2(n_2)\ldots N(n_N) \right]^{\star} \left[\sum_{\{n_i'\}} 1(n_1')2(n_2')\ldots N(n_N') \right] d\tau_1 \ldots d\tau_N$$

where $\{n_i\}$ refers to one of $N!$ combinations of N electrons and the sum is over all $N!$ of these. There are $N!$ additive terms in $[\cdots]^{\star}$ and $N!$ additive terms in $[\cdots]$. But the only non–zero terms after integration are those for which the ordered set $\{n_i\}$ is identical to the ordered set $\{n_i'\}$. Each of these non-zero terms is a normalization integral, so we get $(1)^N = 1$. So, for each of the $N!$ additive terms in $[\cdots]^{\star}$ there is a perfect match with only one of the additive terms in $[\cdots]$. Thus, since

$$|\psi_N\rangle = [N!]^{-1/2}|1, 2, \cdots N|,$$

the result is that

$$c \langle \psi_N | \psi_N \rangle = c[N!]^{-1/2}[N!]^{-1/2}[N!]$$

$$= c.$$

This is exactly what one would expect for a zero-electron operator matrix element between non–anti–symmeterized basis states. Note that all $\Delta so \neq 0$ matrix elements are obviously zero by orthogonality of at least one pair of one-electron spin-orbitals.

(2) One-electron Operators

The selection rule for non-zero matrix elements of a one-electron operator is $\Delta so = 0$ or 1. These two possibilities are discussed separately.

(2A) $\Delta so = 0$

For example, $\widehat{O}p(1) = \hat{S}_z = \sum_i \hat{s}_{z,i}$.

$$\left\langle \psi_N \left| \sum_i \hat{s}_{z,i} \right| \psi \right\rangle = \int \sum_{\{n_i\},\{n_i'\}} \langle n_i | \hat{s}_{z,i} | n_i \rangle \prod_{j \neq i} n_j | n_j' \rangle \, d\tau_1 \ldots d\tau_N.$$

The only non–zero matrix elements are for $\{n_i\} = \{n_i'\}$. For each $\{n_i\}$ term there is only one term from the sum over $\{n'\}$ and there are $N!$ additive terms from the sum over $\{n_i\}$, each one being $\langle n_i | \hat{s}_{z,i} | n_i \rangle \cdot 1 \cdot 1 \cdot 1 \cdots 1$. The sum over $\{n_i\}$ gives $\hbar \sum_{i=1}^N m_{s,i}$. So we have

$$\left\langle \psi_N | \hat{S}_z | \psi_N \right\rangle = \hbar \sum_{i=1}^N m_{s,i} = \hbar M_s$$

which is exactly what one would expect for a non-anti-symmeterized ψ_N.

(2B) $\Delta so = 1$, for example

$$\hat{S}_+ = \sum_{i=1}^N \hat{s}_{+,i}.$$

Here we need a notational trick. Let us label the spin-orbitals in common between ψ_N and ψ_N' as $1 \ldots N$, but label the unique pair of one-electron spin-orbitals as a and b,

$$\Psi_N = (N!)^{-1/2} |12 \cdots a \cdots N|$$
$$\Psi_N' = (N!)^{-1/2} |1 \cdots b \cdots 2 \cdots N|$$

where the spin-orbitals are organized in some agreed-upon standard order. The first task is to rearrange ψ_N' so that the b spin–orbital appears in the same position as the a spin-orbital of ψ_N. This requires a total of p permutations of pairs of spin-orbitals, for example

$$\Psi_N = (4!)^{-1/2} |1a34|$$
$$\Psi_N' = (4!)^{-1/2} |134b|.$$

The sequence of two permutations $[134b| \rightarrow |13b4| \rightarrow |1b34|]$ is needed to put b in the second position of Ψ_N to match the position of a in Ψ_N, hence $p = 2$ and $|1b34| = (-1)^2 |134b|$.

So now we know that the one–electron operator is pinned to the position that connects the a and b spin-orbitals. Any other position would result in orthogonality $\langle a | b \rangle = 0$, or

$\langle N|b\rangle \langle N'|a\rangle = 0$. So now we have $(N-1)!$ arrangements of the matching orbitals and N terms with one of the N electrons in the $\langle a(i)|s_{+,i}|b(i)\rangle$ location. The result is that

$$\left\langle \psi_N|\hat{S}_+|\psi'_N\right\rangle = (-1)^p \langle a|\hat{s}_+|b\rangle$$

where $|a\rangle = |a\alpha\rangle$ and $|b\rangle = |a\beta\rangle$, and the overall matrix element (for this example) is

$$\left\langle \psi_N|\hat{S}_+|\psi'_N\right\rangle = (-1)^p \hbar [S(S+1) - M_S(M_S+1)]^{1/2} \delta_{M+1,M'}.$$

(3) Two–Electron Operators

The selection rule for non-zero matrix elements of a two-electron operator is $\Delta so = 0, 1$ or 2. These three possibilities are discussed separately.

(3A) $\Delta so = 2$ for $\frac{e^2}{r_{ij}}$

The two unique *so*'s in ψ_N are a and b and those in ψ'_N are c and d. The *only* non-zero matrix elements are of the form

$$\left| ab12\cdots N-2 \left| \frac{1}{r_{12}} \right| cd12\cdots N-2 \right|$$

$$\left| ab12\cdots N-2 \left| \frac{1}{r_{12}} \right| dc12\cdots N-2 \right|.$$

We must apply a series of pairwise *so* permutations to the order of *so*'s in ψ'_N so that cd are at the same location as ab in ψ_N, and all of the in-common *so*'s are in standard order, thus we get a $(-1)^{p+p'}$ permutation factor (from the antisymmetric nature of the ψ N-electron basis states). There are $(N-2)!$ ways of arranging the $N-2$ $\psi_N \leftrightarrow \psi'_N$ matched spin-orbitals in ψ_N, each of which picks out only one of the $(N-2)!$ additive terms in ψ'_N. Thus we get a factor of $(N-2)!$ from the matching spin orbitals. We also get a factor of $N(N-1)$ from the number of ways we can assign N electrons to the a and b *so*'s. So the overall matrix element is multiplied by the factor

$$(N!)^{-1/2}(N!)^{-1/2}N(N-1)(N-2)! = 1,$$

and the $\Delta so = 2$ matrix element is

$$(-1)^{p+p'} \left[\left\langle ab \left| \frac{1}{r_{12}} \right| cd \right\rangle - \left\langle ab \left| \frac{1}{r_{12}} \right| dc \right\rangle \right],$$

where the minus sign between the two terms comes from the difference by 1 in the number of pair permutations to put ψ_N' into the $|cd\rangle$ vs. $|dc\rangle$ form. Note that if $m_{s,a} + m_{s,b} \neq m_{s,c} + m_{s,d}$, both matrix elements are zero because $[1/r_{ij}, \hat{S}_z] = 0$ and M_S for ab would be different from that for cd. If ab are $a\alpha b\alpha$ and cd are $c\alpha d\alpha$, both integrals are non-zero but not equal to each other because the spatial part of the integrands, $a(1)c(1)\frac{1}{r_{12}}b(2)d(2) \neq a(1)d(1)\frac{1}{r_{12}}b(2)c(2)$. If ab are $a\alpha b\beta$ and cd are $c\alpha d\beta$, then $\left\langle ab \left| \frac{1}{r_{12}} \right| cd \right\rangle \neq 0$ but $\left\langle ab \left| \frac{1}{r_{12}} \right| dc \right\rangle = 0$ because of α, β orthogonality.

This $\Delta so = 2$ case is relevant to the $1s\alpha 2s\beta \pm 1s\beta 2s\alpha$ example where we need two Slater determinants to describe the two $M_S = 0$ states that give rise to $S = 1$, $M_S = 0$ (triplet) and $S = 0$ (singlet) states. For example,

$$ab \equiv 1s\alpha 2s\beta, cd = 1s\beta 2s\alpha$$

then

$$\left\langle ab \left| \frac{1}{r_{12}} \right| cd \right\rangle = 0 \qquad (\text{mismatched } \alpha, \beta)$$

$$\left\langle ab \left| \frac{1}{r_{12}} \right| dc \right\rangle = J_{1s2s} \neq 0 \qquad (\text{matched } \alpha, \beta)$$

$$\psi_{S=0} = 2^{-1/2}[|ab| - |cd|]$$

$$\psi_{S=1} = 2^{-1/2}[|ab| + |cd|]$$

$$\left\langle \psi_{S=0} \left| \frac{1}{r_{12}} \right| \psi_{S=0} \right\rangle = \frac{1}{2} \left[J_{ab} - K_{ab} + J_{cd} - K_{cd} - 2 \left\langle |ab| \left| \frac{1}{r_{12}} \right| |cd| \right\rangle \right]$$

$$J_{ab} = J_{cd} = J_{1s2s}$$

$$K_{ab} = K_{cd} = 0 \quad (\text{because } \langle \alpha | \beta \rangle = 0)$$

$$|ab| = 2^{-1/2}[a(1)b(2) - a(2)b(1)]$$

$$|cd| = 2^{-1/2}[c(1)d(2) - c(2)d(1)]$$

$$\left\langle |ab| \left| \frac{1}{r_{12}} \right| cd| \right\rangle = \frac{1}{2} \int \left[a(1)b(2)\frac{1}{r_{12}}c(1)d(2) - a(1)b(2)\frac{1}{r_{12}}d(1)c(2) \right.$$

$$\left. - a(2)b(1)\frac{1}{r_{12}}c(1)d(2) + a(2)b(1)\frac{1}{r_{12}}c(2)d(1) \right] d\tau_1 d\tau_2$$

$$= \frac{1}{2} \int \left[0 - a(1)b(2)\frac{1}{r_{12}}d(1)c(2) - a(2)b(1)\frac{1}{r_{12}}c(1)d(2) + 0 \right] d\tau_1 d\tau_2$$

$$= \frac{1}{2}[-K_{1s2s} - K_{1s2s}] = -K_{1s2s}$$

thus

$$\left\langle \psi_{S=0} \left| \frac{1}{r_{12}} \right| \psi_{S=0} \right\rangle = \frac{1}{2}(K_{1s2s} + K_{1s2s}) = K_{1s2s}$$

and

$$\left\langle \psi_{S=1} \left| \frac{1}{r_{12}} \right| \psi_{S=1} \right\rangle = -\frac{1}{2}(K_{1s2s} + K_{1s2s}) = -K_{1s2s}$$

(3B) $\Delta so = 1$

The unique *so* in ψ_N is a and the unique *so* in ψ'_N is b. The common *so*'s are $1, 2, \ldots N-1$. The non-zero non-anti-symmetrized matrix elements have the form

$$\left\langle a(1)1(2) | \hat{O}p | b(1)1(2) \right\rangle$$

and

$$\left\langle a(1)1(2) | \hat{O}p | 1(1)b(2) \right\rangle .$$

The number of binary permutations to put the ψ_N and ψ'_N *so*'s into the required order differs by 1 for the two above contributions to the $\left\langle \psi_N | \hat{O}p | \psi'_N \right\rangle$ Slater determinantal matrix element, thus these two non-anti-symmetrized terms contribute with opposite signs.

There are $(N-2)!$ ways of arranging the $N-2$ matching *so*'s in ψ_N and ψ'_N, $N-1$ choices of the matching *so* that is paired with the unique a or b *so* in the overall matrix element, and N choices of which electron goes into the a *so*. Thus the $\left\langle \psi_N | \hat{O}p | \psi'_N \right\rangle$ matrix element consists of a sum of $N - 1$ $2 - e^-$ matrix elements of the form

$$\left[\left\langle ai | \hat{O}p | bi \right\rangle - \left\langle ai | \hat{O}p | ib \right\rangle \right]$$

and the normalization factor for each pair of terms is

$$(N!)^{-1}(N-2)!N = \frac{1}{N-1}$$

thus

$$\left\langle \psi_N | \hat{O}p | \psi'_N \right\rangle = \frac{1}{N-1} \sum_{i=1}^{N-1} \left[\left\langle ai | \hat{O}p | bi \right\rangle - \left\langle ai | \hat{O}p | ib \right\rangle \right] .$$

(3C) $\Delta so = 0$ (for $1/r_{ij}$ as an example)

This is the most interesting case and also the one that embodies the most important difference from the non-anti-symmetrized case. We have non-zero matrix elements of the form

$$\sum_{i>j=1}^{N} \left[\left\langle ij \left| \frac{1}{r_{12}} \right| ij \right\rangle - \left\langle ij \left| \frac{1}{r_{12}} \right| ji \right\rangle \right].$$

There are $(N-2)!$ ways to arrange the $N-2$ spin-orbitals in ψ_N that are not directly involved in the $\frac{1}{r_{12}}$ integral, and the corresponding $N-2$ spin-orbitals in $\langle \psi_N |$ must be ordered in the same way as those in $|\psi_N\rangle$. There are N equivalent choices for the electron in the ith so and $N-1$ equivalent choices for the electron in the jth so. Thus the $\left\langle \psi_N | \frac{1}{r_{12}} | \psi_N \right\rangle \Delta so = 0$ matrix element reduces to $\sum_{i>j=1}^{N} (J_{ij} - K_{ij})$ Coulomb and exchange integrals. All of the K_{ij} terms are unanticipated from consideration of only the non-anti-symmetrized basis states. The following examples should be easily predicted.

Example	$\left\langle \psi_N | \frac{1}{r_{12}} | \psi_N \right\rangle$
$1s^2$	J_{1s^2} ($K_{1s^2} = 0$ because $\langle \alpha | \beta \rangle = 0$)
$1s\alpha 2s\alpha$	$J_{1s2s} - K_{1s2s}$ (triplet: $S = 1$)
$1s\alpha 2s\beta$ or $1s\beta 2s\alpha$ $\boxed{S = 1}$	J_{1s2s}
$2^{-1/2}[|1s\alpha 2s\beta| \pm 1|1s\beta 2s\alpha|]^{\#}$	$J_{1s2s} + K_{1s2s}$ for $S = 0$
$\boxed{S = 0}$	$J_{1s2s} - K_{1s2s}$ for $S = 1$
$1s^2 2s\alpha$	$J_{1s^2} + 2J_{1s2s} - K_{1s2s}$
$1s^2 2s\alpha^2$	$J_{1s^2} + J_{2s^2} + 4J_{1s2s} - 2K_{1s2s}$
	(sum over all pairs of so's)

\# the K_{1s2s} part of this example comes from the $\Delta so = 2$ terms discussed in section 3A.

4. Shielding

Note that the energy of each S, M_S state that belongs to the configuration $\{n\ell_1, n_2\ell_2, \dots\}$ is given by the sum of the Hydrogenic orbital energies plus the appropriate combination of

$J_{n\ell n'\ell'}$ and $K_{n\ell n'\ell'}$ terms, for example

$$1s2s\ ^3S: \quad -\frac{Z^2}{1^2} - \frac{Z^2}{2^2} + J_{1s2s} - K_{1s2s}$$

$$1s2s\ ^1S: \quad -\frac{Z^2}{1^2} - \frac{Z^2}{2^2} + J_{1s2s} + K_{1s2s}$$

When there are more than 2 electrons present, there will be a large number of J and K terms. For example

$$1s^2 2s^2 3s\alpha\ ^2S$$

$$E(^2S) = 2E_{1s} + 2E_{2s} + E_{3s} + [J_{1s^2} + J_{2s^2} + 4J_{1s2s} - 2K_{1s2s}] + [2J_{1s3s} - K_{1s3s} + 2J_{2s3s} - K_{2s3s}].$$

Note that E_{3s} is negative whereas $[2J_{1s3s} - K_{1s3s} + 2J_{2s3s} - K_{2s3s}]$ is positive. It is tempting to think of this term in $[\cdots]$ as shielding the electron in the $3s$ orbital from the full $+Z$ charge on the nucleus. This leads us to the concept of $Z_{\text{eff}}(r)$ and to the expectaiton values of $Z_{\text{eff}}(r)$ for different values of ℓ (owing to the $+\frac{\ell(\ell+1)}{2r^2}$ centrifugal term in $V_\ell^{\text{eff}}(r)$)

$$\langle n\ell | Z_{\text{eff}} | n\ell \rangle = Z_{\text{eff},\ell} < Z.$$

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