Slater-Condon Rules

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Contents

1 Introduction

1.1 Slater-Condon Rules

The goal of this handout is to prove the following 7 statements about the expectation values of 1- and 2- particle operators with respect to an arbitrary Slater determinant $|\Phi\rangle$ We'll prove them in two different formalisms - first quantization (11 pages) and second quantization (1 page).

For 1-particle operators:

Let $\hat{\mathbf{h}}$ be a 1-particle operator, $\hat{\mathbf{h}} = \sum_i^n \hat{h}_i$.

1. Same determinant
$$\langle\Phi| \hat{\mathbf{h}} |\Phi\rangle = \sum_i \langle\psi_i| \hat{h} |\psi_i\rangle \tag{1}$$

2. Singly excited determinant
$$\langle\Phi| \hat{\mathbf{h}} |\Phi_i^a\rangle = \langle\psi_i| \hat{h} |\psi_a\rangle \tag{2}$$

3. Doubly excited determinant
$$\langle\Phi| \hat{\mathbf{h}} |\Phi_{ij}^{ab}\rangle = 0 \tag{3}$$

For 2-particle operators:

Let $\hat{\mathbf{g}}$ be a 2-particle operator, $\hat{\mathbf{g}} = \sum_{i<j}^n \hat{g}_{ij} = \frac{1}{2}\sum_{i,j}^n \hat{g}_{ij}$.

1. Same determinant
$$\langle\Phi| \hat{\mathbf{g}} |\Phi\rangle = \frac{1}{2}\sum_{ij} \left(\langle\psi_i\psi_j| \hat{g}_{ij} |\psi_i\psi_j\rangle - \langle\psi_i\psi_j| \hat{g}_{ij} |\psi_j\psi_i\rangle\right) \tag{4}$$

2. Singly excited determinant
$$\langle\Phi| \hat{\mathbf{g}} |\Phi_i^a\rangle = \sum_j \left(\langle\psi_i\psi_j| \hat{g}_{ij} |\psi_a\psi_j\rangle - \langle\psi_i\psi_j| \hat{g}_{ij} |\psi_j\psi_a\rangle\right) \tag{5}$$

3. Doubly excited determinant
$$\langle\Phi| \hat{\mathbf{g}} |\Phi_{ij}^{ab}\rangle = \langle\psi_i\psi_j| \hat{g}_{ij} |\psi_a\psi_b\rangle - \langle\psi_i\psi_j| \hat{g}_{ij} |\psi_b\psi_a\rangle \tag{6}$$

4. Triply excited determinant
$$\langle\Phi| \hat{\mathbf{g}} |\Phi_{ijk}^{abc}\rangle = 0 \tag{7}$$

1.2 Important Notation for First Quantization

$\Phi = \frac{1}{\sqrt{n!}}\sum_{i=1}^{n!}(-1)^{p_i}\,\mathcal{P}_i\left(\psi_1(1)...\psi_n(n)\right)$ is a Slater determinant. (By convention, $\langle\psi_i\,|\,\psi_j\rangle = \delta_{ij}$.)

$\mathcal{P}_i$ is a permutation operator that runs over all n! permutations of electrons 1 ... n.

p_i is the number of transpositions required to restore a given permutation to its natural order 1 ... n.

2 Useful Lemmata

Here we prove two Lemmata that follow from the fact that electrons are indistinguishable.

2.1 Lemma for 1-particle operators

Statement: For a one-electron operator $\hat{\mathbf{h}}$,

$$\langle \Phi_P | \sum_{k=1}^{n} \hat{h}_k | \Phi_Q \rangle = n \langle \Phi_P | \hat{h}_1 | \Phi_Q \rangle \;\; \forall \, P, \, Q. \tag{8}$$

Proof:

Since dummy variables are interchangeable in integration,

$$\int \mathrm{d}(1...k...n) \, \Phi_P^*(1...k...n) \, \hat{h}_k \, \Phi_Q(1...k...n) = \int \mathrm{d}(k...1...n) \, \Phi_P^*(k...1...n) \, \hat{h}_1 \, \Phi_Q(k...1...n)$$

Furthermore, since the order of the differential elements themselves does not matter,

$$= \int \mathrm{d}(1...k...n) \, \Phi_P^*(k...1...n) \, \hat{h}_1 \, \Phi_Q(k...1...n)$$

Now applying the antisymmetry property of determinants,

$$\begin{aligned}
&= (-1) \int \mathrm{d}(1...k...n) \, \Phi_P^*(1...k...n) \, \hat{h}_1 \, \Phi_Q(k...1...n) \\
&= (-1)^2 \int \mathrm{d}(1...k...n) \, \Phi_P^*(1...k...n) \, \hat{h}_1 \, \Phi_Q(1...k...n) \\
&= \int \mathrm{d}(1...k...n) \, \Phi_P^*(1...k...n) \, \hat{h}_1 \, \Phi_Q(1...k...n)
\end{aligned}$$

Rewriting in Dirac notation, what we have shown is that

$$\langle \Phi_P | \hat{h}_k | \Phi_Q \rangle = \langle \Phi_P | \hat{h}_1 | \Phi_Q \rangle .$$

We can easily apply this result to the sum over all electrons in the system:

$$\begin{aligned}
\langle \Phi_P | \sum_{k=1}^{n} \hat{h}_k | \Phi_Q \rangle &= \sum_{k=1}^{n} \langle \Phi_P | \hat{h}_k | \Phi_Q \rangle \\
&= \sum_{k=1}^{n} \langle \Phi_P | \hat{h}_1 | \Phi_Q \rangle \\
&= n \langle \Phi_P | \hat{h}_1 | \Phi_Q \rangle .
\end{aligned}$$

To recapitulate, this lemma states that since determinants do not distinguish between identical electrons, matrix elements of $h(\hat{1})$ will be indistinguishable from $h(\hat{2})$, $h(\hat{3})$, etc. So if $\hat{\mathbf{h}}$ is a one-electron operator acting on electrons $1, ..., n$, we need only calculate the expectation value of $\hat{h}_1$ and multiply times n.

2.2 Lemma for 2-particle operators

Statement: For a two-electron operator $\hat{\mathbf{g}}$,

$$\langle\Phi_P|\sum_{j<k}^{n}\hat{g}_{jk}\;|\Phi_Q\rangle = \frac{n(n-1)}{2}\langle\Phi_P|\;\hat{g}_{12}\;|\Phi_Q\rangle\;\;\forall\, P,\, Q. \tag{9}$$

Proof:

By the same logic as 1.1.1, we use the interchangeability of dummy variables and antisymmetry of determinants.

$$\int \mathrm{d}(1,2...j,k...n)\,\Phi_P^*(1,2...j,k...n)\,\hat{g}(j,k)\,\Phi_Q(1,2...j,k...n) =$$
$$= \int \mathrm{d}(j,k...1,2...n)\,\Phi_P^*(j,k...1,2...n)\,\hat{g}_{12}\,\Phi_Q(j,k...1,2...n)$$

Since dummy variables are interchangeable in integration,

$$\begin{aligned}
&= \int \mathrm{d}(1,2...j,k...n)\Phi_P^*(j,k...1,2...n)\,\hat{g}_{12}\,\Phi_Q(j,k...1,2...n)\\
&= -\int \mathrm{d}(1,2...j,k...n)\Phi_P^*(j,2...1,k...n)\,\hat{g}_{12}\,\Phi_Q(j,k...1,2...n)\\
&= \int \mathrm{d}(1,2...j,k...n)\Phi_P^*(1,2...j,k...n)\,\hat{g}_{12}\,\Phi_Q(j,k...1,2...n)\\
&= \int \mathrm{d}(1,2...j,k...n)\Phi_P^*(1,2...j,k...n)\,\hat{g}_{12}\,\Phi_Q(1,2...j,k...n)
\end{aligned}$$

Rewriting in Dirac notation, what we have shown is that

$$\langle\Phi_p|\,\hat{g}_{jk}\,|\Phi_Q\rangle = \langle\Phi_P|\,\hat{g}_{12}\,|\Phi_q\rangle\,.$$

We can easily apply this result to the sum over all distinct pairs of electrons in the system:

$$\begin{aligned}
\langle\Phi_P|\sum_{j<k}^{n}\hat{g}_{jk}\,|\Phi_Q\rangle &= \sum_{j<k}^{n}\langle\Phi_P|\,\hat{g}_{jk}\,|\Phi_Q\rangle\\
&= \sum_{j<k}^{n}\langle\Phi_P|\,\hat{g}_{12}\,|\Phi_Q\rangle\\
&= \frac{n(n-1)}{2}\langle\Phi_P|\,\hat{g}_{12}\,|\Phi_Q\rangle\,.
\end{aligned}$$

In words, this lemma states that since the electrons in a determinant are indistinguishable, each of the terms in the sum over pairs of indices j and k will give the same result. Therefore we can replace $\hat{g}_{ij}$ with $\hat{g}_{12}$ and multiply times the total number of pairs of electrons, which is $\frac{n(n-1)}{2}$.

3 1-particle operator proofs (1st quantization)

3.1 Same determinant

To show: $\langle\Phi|\,\hat{\mathbf{h}}\,|\Phi\rangle = \sum_i \langle\psi_i|\,\hat{h}\,|\psi_i\rangle$.

Expanding the determinants Φ in terms of the permutation operator,

$$\begin{aligned}
\langle\Phi|\,\hat{\mathbf{h}}\,|\Phi\rangle &= \frac{1}{n!}\left\langle \sum_{\pi}^{n!}(-1)^{p_\pi}\mathcal{P}_\pi\left(\psi_1(1)...\psi_n(n)\right)\middle|\sum_{k=1}^{n}\hat{h}(k)\middle|\sum_{\sigma}^{n!}(-1)^{p_\sigma}\mathcal{P}_\sigma\left(\psi_1(1)...\psi_n(n)\right)\right\rangle \\
&= \frac{1}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi\left(\psi_1(1)...\psi_n(n)\right)\right|\sum_{k=1}^{n}\hat{h}(k)\left|\mathcal{P}_\sigma\left(\psi_1(1)...\psi_n(n)\right)\right\rangle
\end{aligned}$$

By lemma 2.1,

$$= \frac{n}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi\left(\psi_1(1)...\psi_n(n)\right)\right|\hat{h}_1\left|\mathcal{P}_\sigma\left(\psi_1(1)...\psi_n(n)\right)\right\rangle$$

Next apply orthogonality of the spin orbitals: In the integration over electrons 2,3,...n, we will obtain zero unless all $n-1$ of these electrons occupy the same spin orbitals in $\mathcal{P}_\pi$ as they do in $\mathcal{P}_\sigma$. By the pigeon-hole principle, then, electron 1 must occupy the same spin orbital in both permutations as well. In other words, $\mathcal{P}_\sigma = \mathcal{P}_\pi$.

$$\begin{aligned}
&= \frac{1}{(n-1)!}\sum_{\pi,\sigma}^{n!}\delta_{\pi,\sigma}\,(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi\left(\psi_1(1)...\psi_n(n)\right)\right|\hat{h}_1\left|\mathcal{P}_\sigma\left(\psi_1(1)...\psi_n(n)\right)\right\rangle \\
&= \frac{1}{(n-1)!}\sum_{\pi}^{n!}(-1)^{2p_\pi}\left\langle\mathcal{P}_\pi\left(\psi_1(1)...\psi_n(n)\right)\right|\hat{h}_1\left|\mathcal{P}_\pi\left(\psi_1(1)...\psi_n(n)\right)\right\rangle \\
&= \frac{1}{(n-1)!}\sum_{k=1}^{n}\left\langle\psi_k(1)\middle|\hat{h}_1\middle|\psi_k(1)\right\rangle\sum_{\rho}^{(n-1)!}\left\langle\mathcal{P}_\rho\left(\psi_1(2)...\cancel{\psi_k(1)}...\psi_n(n)\right)\middle|\mathcal{P}_\rho\left(\psi_1(2)...\cancel{\psi_k(1)}...\psi_n(n)\right)\right\rangle
\end{aligned}$$

Since the basis is orthonormal, all of the nonzero overlap integrals will introduce a factor of 1.

$$\begin{aligned}
&= \frac{1}{(n-1)!}\sum_{k=1}^{n}\langle\psi_k(1)|\,\hat{h}_1\,|\psi_k(1)\rangle\sum_{i=1}^{(n-1)!}\mathcal{P}_\rho(\delta_{11}\delta_{22}...\cancel{\delta_{kk}}...\delta_{nn}) \\
&= \frac{1}{(n-1)!}\sum_{k=1}^{n}\langle\psi_k(1)|\,\hat{h}_1\,|\psi_k(1)\rangle\sum_{i=1}^{(n-1)!}(1) \\
&= \frac{1}{(n-1)!}\sum_{k=1}^{n}\langle\psi_k(1)|\,\hat{h}_1\,|\psi_k(1)\rangle\ (n-1)! \\
&= \sum_{k=1}^{n}\langle\psi_k|\,\hat{h}\,|\psi_k\rangle
\end{aligned}$$

$\blacksquare$.

3.2 Singly excited determinant

To show: $\langle\Phi|\,\hat{\mathbf{h}}\,|\Phi_i^a\rangle = \langle\psi_i|\,\hat{h}\,|\psi_a\rangle$.

Expanding Φ in terms of the permutation operator,

$$\begin{aligned}
\langle\Phi|\,\hat{\mathbf{h}}\,|\Phi_i^a\rangle &= \frac{1}{n!}\left\langle \sum_{\pi}^{n!}(-1)^{p_\pi}\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_n(n)) \middle| \sum_{k=1}^{n}\hat{h}(k) \middle| \sum_{\sigma}^{n!}(-1)^{p_\sigma}\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_n(n))\right\rangle \\
&= \frac{1}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\,\langle\mathcal{P}_\pi\,(\psi_1(1)...\psi_i(i)...\psi_n(n))|\sum_{k=1}^{n}\hat{h}(k)\,|\mathcal{P}_\sigma\,(\psi_1(1)...\psi_a(i)...\psi_n(n))\rangle
\end{aligned}$$

By lemma 2.1,

$$= \frac{n}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\,\langle\mathcal{P}_\pi\,(\psi_1(1)...\psi_i(i)...\psi_n(n))|\,\hat{h}_1\,|\mathcal{P}_\sigma\,(\psi_1(1)...\psi_a(i)...\psi_n(n))\rangle$$

Now we employ orthogonality of the spin orbitals. Note that spin orbitals ψ_i in the first determinant and ψ_a in the second determinant are each orthogonal to every other spin orbital in the opposite determinant. This means that any integral containing the overlap $\langle\psi_i(j)|\psi_k(j)\rangle$ or $\langle\psi_k(j)|\psi_a(j)\rangle$ will vanish for electron j in any possible ψ_k. The only way to avoid this is to have electron 1 in orbital ψ_i in the first determinant and ψ_a in the second determinant.

$$= \frac{1}{(n-1)!}\sum_{\pi,\sigma}^{(n-1)!}(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi\left(\psi_1(2)...\cancel{\psi_i(1)}...\psi_n(n)\right)\middle|\,\mathcal{P}_\sigma\left(\psi_1(2)...\cancel{\psi_a(1)}...\psi_n(n)\right)\right\rangle\langle\psi_i(1)|\,\hat{h}_1\,|\psi_a(1)\rangle$$

Because the spin orbitals are orthonormal, each integral will vanish unless $\mathcal{P}_\pi = \mathcal{P}_\sigma$.

$$\begin{aligned}
&= \langle\psi_i(1)|\,\hat{h}_1\,|\psi_a(1)\rangle\,\frac{1}{(n-1)!}\sum_{r=1}^{(n-1)!}(-1)^{2p_\pi}\left\langle\mathcal{P}_\pi\left(\psi_1(1)...\cancel{\psi_i(i)}...\psi_n(n)\right)\middle|\,\mathcal{P}_\pi\left(\psi_1(1)...\cancel{\psi_a(i)}...\psi_n(n)\right)\right\rangle \\
&= \langle\psi_i(1)|\,\hat{h}_1\,|\psi_a(1)\rangle\,\frac{1}{(n-1)!}\sum_{r=1}^{(n-1)!}\mathcal{P}_\pi(\delta_{11}\delta_{22}...\cancel{\delta_{ia}}...\delta_{nn}) \\
&= \langle\psi_i(1)|\,\hat{h}_1\,|\psi_a(1)\rangle\,\frac{1}{(n-1)!}\sum_{r=1}^{(n-1)!}1 \\
&= \langle\psi_i(1)|\,\hat{h}_1\,|\psi_a(1)\rangle\,\frac{1}{(n-1)!}\,(n-1)! \\
&= \langle\psi_i|\,\hat{h}\,|\psi_a\rangle
\end{aligned}$$

$\blacksquare$.

3.3 Doubly excited determinant

To show: $\langle\Phi|\,\hat{\mathbf{h}}\,|\Phi_{ij}^{ab}\rangle = 0$.

Expanding Φ in terms of the permutation operator,

$$\langle\Phi|\,\hat{\mathbf{h}}\,\big|\Phi_{ij}^{ab}\big\rangle =$$

$$=\frac{1}{n!}\left\langle\sum_{\pi}^{n!}(-1)^{p_\pi}\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_n(n))\right|\sum_{\pi}^{n}\hat{h}(k)\left|\sum_{\sigma}^{n!}(-1)^{p_\sigma}\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_n(n))\right\rangle$$

$$=\frac{1}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_n(n))\right|\sum_{\pi}^{n}\hat{h}(k)\left|\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_n(n))\right\rangle$$

By lemma 2.1,

$$=\frac{n}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_n(n))\right|\hat{h}_1\left|\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_n(n))\right\rangle$$

Now by the same logic used in section 3.2, any integral containing the overlap $\langle\psi_i(j)|\psi_k(j)\rangle$ or $\langle\psi_k(j)|\psi_a(j)\rangle$ will vanish for electron j in any possible ψ_k. Again the only way to avoid this is to have electron 1 in orbital ψ_i in the first determinant and ψ_a in the second determinant.

$$=\frac{1}{(n-1)!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\Big\langle\mathcal{P}_\pi(\psi_1(3)...\cancel{\psi_i(1)}...\psi_j(2)...\psi_n(n))\,\Big|\,\mathcal{P}_\sigma(\psi_1(3)...\cancel{\psi_a(1)}...\psi_b(2)...\psi_n(n))\Big\rangle\,\langle\psi_i|\,\hat{h}\,|\psi_a\rangle$$

However, this time there are still two spin orbitals ψ_j in $\mathcal{P}_\pi$ and ψ_b in $\mathcal{P}_\sigma$ such that $\langle\psi_j(j)|\psi_k(j)\rangle$ or $\langle\psi_k(j)|\psi_b(j)\rangle$ will vanish for electron j in any other ψ_k in the determinant. Therefore, no matter how we permute these two determinants, all $(n-1)!^2$ integrals will have at least one zero overlap that causes it to vanish.

$$= 0$$

$\blacksquare$.

4 2-particle operator proofs (1st quantization)

4.1 Same determinant

To show: $\langle\Phi|\,\hat{\mathbf{g}}(i,j)\,|\Phi\rangle = \sum_{i<j}\left(\langle\psi_i\psi_j|\,\hat{g}_{ij}\,|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\,\hat{g}_{ij}\,|\psi_j\psi_i\rangle\right)$.

$$
\begin{aligned}
\langle\Phi|\;\hat{\mathbf{g}}\;|\Phi\rangle =& \frac{1}{n!}\left\langle \sum_{\pi}^{n!}(-1)^{p_\pi}\mathcal{P}_\pi(\psi_1(1)...\psi_n(n))\right|\sum_{i<j}^{n}\hat{g}_{ij}\left|\sum_{\sigma}^{n!}(-1)^{p_\sigma}\mathcal{P}_\sigma(\psi_1(1)...\psi_n(n))\right\rangle \\
=& \frac{1}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\;\langle\mathcal{P}_\pi(\psi_1(1)...\psi_n(n))|\sum_{i<j}^{n}\hat{g}_{ij}\;|\mathcal{P}_\sigma(\psi_1(1)...\psi_n(n))\rangle \\
=& \frac{n(n-1)}{2n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\;\langle\mathcal{P}_\pi(\psi_1(1)...\psi_n(n))|\;\hat{g}_{12}\;|\mathcal{P}_\sigma(\psi_1(1)...\psi_n(n))\rangle\quad\text{(by lemma 2.2).}
\end{aligned}
$$

Since $\hat{g}$ only acts on electrons 1 and 2, we can separate this integral into the sum over all permutations of electrons 1 and 2 multiplied times the sum over all permutations of electrons 3...n in the remaining orbitals:

$$
\begin{aligned}
=& \frac{1}{2(n-2)!}\sum_{i<j}^{n}\left\langle\sum_{\mu}^{2!}(-1)^{p_\mu}\mathcal{P}_\mu(\psi_i(1)\psi_j(2))\right|\hat{g}_{12}\left|\sum_{\nu}^{2!}(-1)^{p_\nu}\mathcal{P}_\nu(\psi_i(1)\psi_j(2))\right\rangle \\
&\cdot\sum_{\pi,\sigma}^{(n-2)!}(-1)^{p_\pi+p_\sigma}\;\left\langle\mathcal{P}_\pi(\psi_1(3)...\cancel{\psi_i(1)}...\cancel{\psi_j(2)}...\psi_n(n))\,\middle|\,\mathcal{P}_\sigma(\psi_1(3)...\cancel{\psi_i(1)}...\cancel{\psi_j(2)}...\psi_n(n))\right\rangle
\end{aligned}
$$

Because the basis set is orthonormal, each overlap integral after the last two summands will vanish unless the permutations $\mathcal{P}_\pi$ and $\mathcal{P}_\sigma$ are identical, so let $\pi=\sigma$.

$$
\begin{aligned}
=& \frac{1}{2(n-2)!}\sum_{i<j}^{n}\sum_{\mu,\nu}^{4}(-1)^{p_\mu+p_\nu}\,\langle\mathcal{P}_\mu(\psi_i(1)\psi_j(2))|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_i(1)\psi_j(2))\rangle\sum_{\pi}^{(n-2)!}(-1)^{2p_\pi}\,\mathcal{P}_\pi(\delta_{11}...\cancel{\delta_{ii}}...\cancel{\delta_{jj}}...\delta_{nn}) \\
=& \frac{(n-2)!}{2(n-2)!}\sum_{i<j}^{n}\sum_{\mu,\nu}^{4}(-1)^{p_\mu+p_\nu}\,\langle\mathcal{P}_\mu(\psi_i(1)\psi_j(2))|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_i(1)\psi_j(2))\rangle
\end{aligned}
$$

Now let's write explicitly the two permutations introduced by $\mathcal{P}_\mu$.

$$
\begin{aligned}
=& \frac{1}{2}\sum_{i<j}^{n}\sum_{\nu}^{2}(-1)^{p_\nu}\left[\langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_i(1)\psi_j(2))\rangle - \langle\psi_i(2)\psi_j(1)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_i(1)\psi_j(2))\rangle\right] \\
=& \frac{1}{2}\sum_{i<j}^{n}\sum_{\nu}^{2}(-1)^{p_\nu}\left[\langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_i(1)\psi_j(2))\rangle - \langle-\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_i(1)\psi_j(2))\rangle\right] \\
=& \frac{1}{2}\sum_{i<j}^{n}\sum_{\nu}^{2}(-1)^{p_\nu}\cdot 2\,\langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_i(1)\psi_j(2))\rangle
\end{aligned}
$$

Now let's write explicitly the two permutations introduced by $\mathcal{P}_\nu$.

$$
\begin{aligned}
=& \sum_{i<j}^{n}\langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\psi_i(1)\psi_j(2)\rangle - \langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\psi_i(2)\psi_j(1)\rangle \\
=& \sum_{i<j}^{n}\langle\psi_i\psi_j|\,\hat{g}_{12}\,|\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\,\hat{g}_{12}\,|\psi_j\psi_i\rangle \\
&\blacksquare.
\end{aligned}
$$

4.2 Singly excited determinant

To show: $\langle\Phi|\,\hat{\mathbf{g}}\,|\Phi_i^a\rangle = \sum_j^n \left(\langle\psi_i\psi_j|\,\hat{g}_{ij}\,|\psi_a\psi_j\rangle - \langle\psi_i\psi_j|\,\hat{g}_{ij}\,|\psi_j\psi_a\rangle\right)$.

$$\begin{aligned}
\langle\Phi|\;\hat{\mathbf{g}}\;|\Phi_i^a\rangle =& \frac{1}{n!}\left\langle \sum_\pi^{n!}(-1)^{p_\pi}\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_n(n)) \middle| \sum_{i<j}^n \hat{g}_{ij} \middle| \sum_\sigma^{n!}(-1)^{p_\sigma}\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_n(n)) \right\rangle \\
=& \frac{1}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_n(n))\right|\sum_{i<j}^n\hat{g}_{ij}\left|\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_n(n))\right\rangle \\
=& \frac{n(n-1)}{2n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_n(n))\right|\hat{g}_{12}\left|\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_n(n))\right\rangle
\end{aligned}$$

First we apply the orthogonality condition of the spin orbitals. Since ψ_i and ψ_a are orthogonal, it must be that either electron 1 or 2 occupies both ψ_i on the left and ψ_a on the right. Suppose electron 1 is occupying ψ_i on the left side of the integral. Then electron 2 can occupy any other ψ_j in the determinant, or vice versa.

$$\begin{aligned}
=& \frac{1}{2(n-2)!}\sum_j^n\left\langle\mathcal{P}_{12}\psi_i(1)\psi_j(2)\right|\hat{g}_{12}\left|\mathcal{P}_{12}\psi_a(1)\psi_j(2)\right\rangle \\
&\cdot\sum_{\pi,\sigma}^{(n-2)!}(-1)^{p_\pi+p_\sigma}\left\langle\mathcal{P}_\pi(\psi_1(3)...\cancel{\psi_i(1)}...\cancel{\psi_j(2)}...\psi_n(n))\,\middle|\,\mathcal{P}_\sigma(\psi_1(3)...\cancel{\psi_a(1)}...\cancel{\psi_j(2)}...\psi_n(n))\right\rangle
\end{aligned}$$

Now this second term is simply a product of overlap integrals of $(n-2)$ electrons; these will vanish except in the permutations which integrate over identical spin orbitals, i.e., when $\mathcal{P}_\pi = \mathcal{P}_\sigma$.

$$\begin{aligned}
=& \frac{1}{2(n-2)!}\sum_j^n\sum_{\mu,\nu}^4(-1)^{p_\mu+p_\nu}\left\langle\mathcal{P}_\mu(\psi_i(1)\psi_j(2))\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle\sum_r^{(n-2)!}(-1)^{2p_\pi}\mathcal{P}_\pi(\delta_{11}...\cancel{\delta_{ia}}...\delta_{nn}) \\
=& \frac{1}{2(n-2)!}\sum_j^n\sum_{\mu,\nu}^4(-1)^{p_\mu+p_\nu}\left\langle\mathcal{P}_\mu(\psi_i(1)\psi_j(2))\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle\sum_r^{(n-2)!}(1) \\
=& \frac{1}{2(n-2)!}(n-2)!\sum_j\sum_{\mu,\nu}^4(-1)^{p_\mu+p_\nu}\left\langle\mathcal{P}_\mu(\psi_i(1)\psi_j(2))\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle \\
=& \frac{1}{2}\sum_j^n\sum_{\mu,\nu}^4(-1)^{p_\mu+p_\nu}\left\langle\mathcal{P}_\mu(\psi_i(1)\psi_j(2))\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle
\end{aligned}$$

Now let's write out explicitly all the permutations introduced by $\mathcal{P}_\mu$.

$$\begin{aligned}
=& \frac{1}{2}\sum_j^n\sum_\nu^2(-1)^{p_\nu}\left[\left\langle\psi_i(1)\psi_j(2)\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle - \left\langle\psi_i(2)\psi_j(1)\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle\right] \\
=& \frac{1}{2}\sum_j^n\sum_\nu^2(-1)^{p_\nu}\left[\left\langle\psi_i(1)\psi_j(2)\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle - \left\langle-\psi_i(1)\psi_j(2)\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle\right] \\
=& \frac{1}{2}\sum_j^n\sum_\nu^2(-1)^{p_\nu}\cdot 2\left\langle\psi_i(1)\psi_j(2)\right|\hat{g}_{12}\left|\mathcal{P}_\nu(\psi_a(1)\psi_j(2))\right\rangle
\end{aligned}$$

Now we can write out explicitly all the permutations introduced by $\mathcal{P}_\nu$.

$$
\begin{aligned}
&= \sum_j^n [\langle \psi_i(1)\psi_j(2)| \, \hat{g}_{12} \, |\psi_a(1)\psi_j(2)\rangle - \langle \psi_i(1)\psi_j(2)| \, \hat{g}_{12} \, |\psi_a(2)\psi_j(1)\rangle] \\
&= \sum_j^n \left(\langle \psi_i\psi_j| \, \hat{g}_{ij} \, |\psi_a\psi_j\rangle - \langle \psi_i\psi_j| \, \hat{g}_{ij} \, |\psi_j\psi_a\rangle \right)
\end{aligned}
$$

4.3 Doubly excited determinant

To show: $\langle \Phi| \, \hat{\mathbf{g}} \, |\Phi_{ij}^{ab}\rangle = \langle \psi_i\psi_j| \, \hat{g}_{12} \, |\psi_a\psi_b\rangle - \langle \psi_i\psi_j| \, \hat{g}_{12} \, |\psi_b\psi_a\rangle$.

Expanding Φ in terms of the permutation operator,

$$
\begin{aligned}
\langle \Phi| \, \hat{\mathbf{g}} \, \left|\Phi_{ij}^{ab}\right\rangle =& \frac{1}{n!} \left\langle \sum_\pi^{n!} (-1)^{p_\pi} \mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_n(n)) \middle| \sum_{i<j}^n \hat{g}_{ij} \middle| \sum_\sigma^{n!} (-1)^{p_\sigma} \mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_n(n)) \right\rangle \\
=& \frac{1}{n!} \sum_{\pi,\sigma}^{n!} (-1)^{p_\pi+p_\sigma} \langle \mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_n(n))| \sum_{i<j}^n \hat{g}_{ij} \, |\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_n(n))\rangle
\end{aligned}
$$

By lemma 2.2,

$$
\begin{aligned}
&= \frac{n(n-1)}{2n!} \sum_{\pi,\sigma}^{n!} (-1)^{p_\pi+p_\sigma} \langle \mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_n(n))| \, \hat{g}_{12} \, |\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_n(n))\rangle \\
&= \frac{1}{2(n-2)!} \sum_{\pi,\sigma}^{n!} (-1)^{p_\pi+p_\sigma} \langle \mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_n(n))| \, \hat{g}_{12} \, |\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_n(n))\rangle
\end{aligned}
$$

Now ψ_i and ψ_j in $\mathcal{P}_\pi$ have a zero overlap with each orbital in $\mathcal{P}_\sigma$. Likewise, orbitals ψ_a and ψ_b in $\mathcal{P}_\sigma$ have a zero overlap with each orbital in $\mathcal{P}_\pi$. Therefore it must be that electrons 1 and 2 must occupy ψ_i and ψ_j in $\mathcal{P}_\pi$ and ψ_a and ψ_b in $\mathcal{P}_\sigma$, in no particular order.

$$
\begin{aligned}
&= \frac{1}{2(n-2)!} \sum_{\mu,\nu}^{4} \langle \mathcal{P}_\mu \psi_i(1)\psi_j(2)| \, \hat{g}_{12} \, |\mathcal{P}_\nu \psi_a(1)\psi_b(2)\rangle \\
&\cdot \sum_{\pi,\sigma}^{(n-2)!} (-1)^{p_\pi+p_\sigma} \left\langle \mathcal{P}_\pi(\psi_1(1)...\cancel{\psi_i(i)}...\cancel{\psi_j(j)}...\psi_n(n)) \right| \hat{g}_{12} \left| \mathcal{P}_\sigma(\psi_1(1)...\cancel{\psi_a(i)}...\cancel{\psi_b(j)}...\psi_n(n)) \right\rangle
\end{aligned}
$$

Because of orthormality, we again let $\mathcal{P}_\pi = \mathcal{P}_\sigma$.

$$
\begin{aligned}
&= \frac{1}{2(n-2)!} \sum_{\mu,\nu}^{4} (-1)^{p_\mu+p_\nu} \langle \mathcal{P}_\mu \psi_i(1)\psi_j(2)| \, \hat{g}_{12} \, |\mathcal{P}_\nu \psi_a(1)\psi_b(2)\rangle \sum_{\pi,\sigma}^{(n-2)!} \mathcal{P}_\pi(\delta_{11}...\delta_{ia}...\delta_{jb}...\delta_{nn}) \\
&= \frac{1}{2(n-2)!} \sum_{\mu,\nu}^{4} (-1)^{p_\mu+p_\nu} \langle \mathcal{P}_\mu \psi_i(1)\psi_j(2)| \, \hat{g}_{12} \, |\mathcal{P}_\nu \psi_a(1)\psi_b(2)\rangle \sum_{\pi,\sigma}^{(n-2)!} (1) \\
&= \frac{1}{2(n-2)!} \sum_{\mu,\nu}^{4} (-1)^{p_\mu+p_\nu} \langle \mathcal{P}_\mu \psi_i(1)\psi_j(2)| \, \hat{g}_{12} \, |\mathcal{P}_\nu \psi_a(1)\psi_b(2)\rangle \, (n-2)!
\end{aligned}
$$

Now let's write out explicitly all the permutations introduced by $\mathcal{P}_\mu$.

$$
\begin{aligned}
=&\frac{1}{2}\sum_{\nu}^{2}(-1)^{p_\nu}\left[\langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_a(1)\psi_b(2))\rangle - \langle\psi_i(2)\psi_j(1)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_a(1)\psi_b(2))\rangle\right]\\
=&\frac{1}{2}\sum_{\nu}^{2}(-1)^{p_\nu}\left[\langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_a(1)\psi_b(2))\rangle - \langle-\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_a(1)\psi_b(2))\rangle\right]\\
=&\frac{1}{2}\sum_{\nu}^{2}(-1)^{p_\nu}\cdot 2\,\langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_a(1)\psi_b(2))\rangle
\end{aligned}
$$

Now we can write out explicitly all the permutations introduced by $\mathcal{P}_\nu$.

$$
\begin{aligned}
&= \langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\psi_a(1)\psi_b(2)\rangle - \langle\psi_i(1)\psi_j(2)|\,\hat{g}_{12}\,|\psi_a(2)\psi_b(1)\rangle\\
&= \langle\psi_i\psi_j|\,\hat{g}_{12}\,|\psi_a\psi_b\rangle - \langle\psi_i\psi_j|\,\hat{g}_{12}\,|\psi_a\psi_b\rangle \quad \blacksquare.
\end{aligned}
$$

4.4 Triply excited determinant

To show: $\langle\Phi|\,\hat{\mathbf{g}}\left|\Phi_{ijk}^{abc}\right\rangle = 0$.

$$
\begin{aligned}
&\langle\Phi|\,\hat{\mathbf{g}}\,\left|\Phi_{ijk}^{abc}\right\rangle =\\
&=\frac{1}{n!}\left\langle\sum_{\pi}^{n!}(-1)^{p_\pi}\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_k(k)...\psi_n(n))\right|\sum_{i<j}^{n}\hat{g}_{ij}\left|\sum_{\sigma}^{n!}(-1)^{p_\sigma}\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_c(k)...\psi_n(n))\right\rangle\\
&=\frac{1}{n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\,\langle\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_k(k)...\psi_n(n))|\sum_{i<j}^{n}\hat{g}_{ij}\,|\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_c(k)...\psi_n(n))\rangle
\end{aligned}
$$

By lemma 2.2,

$$
\begin{aligned}
&=\frac{n(n-1)}{2n!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\,\langle\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_k(k)...\psi_n(n))|\sum_{i<j}^{n}\hat{g}_{ij}\,|\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_c(k)...\psi_n(n))\rangle\\
&=\frac{1}{2(n-2)!}\sum_{\pi,\sigma}^{n!}(-1)^{p_\pi+p_\sigma}\,\langle\mathcal{P}_\pi(\psi_1(1)...\psi_i(i)...\psi_j(j)...\psi_k(k)...\psi_n(n))|\sum_{i<j}^{n}\hat{g}_{ij}\,|\mathcal{P}_\sigma(\psi_1(1)...\psi_a(i)...\psi_b(j)...\psi_c(k)...\psi_n(n))\rangle
\end{aligned}
$$

Since ψ_i and ψ_j in $\mathcal{P}_\pi$ have a zero overlap with each orbital in $\mathcal{P}_\sigma$ and ψ_a and ψ_b in $\mathcal{P}_\sigma$ have a zero overlap with each orbital in $\mathcal{P}_\pi$, it must be that electrons 1 and 2 must occupy ψ_i and ψ_j in $\mathcal{P}_\pi$ and ψ_a and ψ_b in $\mathcal{P}_\sigma$, in no particular order.

$$
\begin{aligned}
&=\frac{1}{2(n-2)!}\sum_{\mu,\nu}^{4}(-1)^{p_\mu+p_\nu}\,\langle\mathcal{P}_\mu(\psi_i(1)\psi_j(2))|\,\hat{g}_{12}\,|\mathcal{P}_\nu(\psi_a(1)\psi_b(2))\rangle\\
&\cdot\sum_{\pi,\sigma}^{(n-2)!}(-1)^{p_\pi+p_\sigma}\,\left\langle\mathcal{P}_\pi(\psi_1(1)...\cancel{\psi_i(i)}...\cancel{\psi_j(j)}...\psi_k(k)...\psi_n(n))\right|\hat{g}_{12}\left|\mathcal{P}_\sigma(\psi_1(1)...\cancel{\psi_a(i)}...\cancel{\psi_b(j)}...\psi_c(k)...\psi_n(n))\right\rangle
\end{aligned}
$$

However, this time there are still two spin orbitals ψ_k in $\mathcal{P}_\pi$ and ψ_c in $\mathcal{P}_\sigma$ that $\langle\psi_k(i)|\psi_i(i)\rangle$ or $\langle\psi_i(i)|\psi_c(i)\rangle$ will vanish for electron in any ψ_i in the opposite determinant. Therefore, no matter how we permute these two determinants, all $(n-1)!^2$ integrals will have at least one zero overlap that causes it to vanish.

$$= 0 \quad \blacksquare.$$