1 Spin-orbital Formalism

The molecular Hamiltonian could be written as:

$$\hat{H} = -\frac{1}{2}\sum_i^{N_{\text{el}}} \nabla_i^2 + \sum_K^{N_{\text{nuc}}}\sum_i^{N_{\text{el}}} \frac{Z_K}{|\mathbf{R}_K - \mathbf{r}_i|} + \sum_{j>i}^{N_{\text{el}}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{K>L}^{N_{\text{nuc}}} \frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|} \tag{1}$$

Alternatively, we could write the electronic part into second-quantized form:

$$\hat{H}_{\text{elec}} = \sum_{pq} h_{pq}\hat{p}^\dagger\hat{q} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r} \tag{2}$$

where we denote the one-electron integral:

$$h_{pq} = \langle p|\hat{h}|q\rangle = \langle p|\Big(-\frac{1}{2}\nabla^2 + \sum_K^{N_{\text{nuc}}} \frac{Z_K}{|\mathbf{R}_K - \mathbf{r}|}\Big)|q\rangle \tag{3}$$

and the anti-symmetrized two-electron integrals:

$$\langle pq||rs\rangle = \langle pq|\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|rs\rangle - \langle pq|\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|sr\rangle \tag{4}$$

In these expressions the electron indices are implicitly carried.
Now to partition the Hamiltonian into reference and perturbation, we firstly expand the expression with Wick's theorm:

$$\hat{H}_{\text{elec}} = \sum_{pq} h_{pq}\{\hat{p}^\dagger\hat{q}\} + \sum_i h_{ii} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} + \sum_{ipq}\langle pi||qi\rangle\{\hat{p}^\dagger\hat{q}\} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \tag{5}$$

We can partition the Hamiltonian into:

$$\begin{aligned}
\hat{H}_{\text{elec}} &= \Big(\sum_{pq} h_{pq}\{\hat{p}^\dagger\hat{q}\} + \sum_{pqi}\langle pi||qi\rangle\{\hat{p}^\dagger\hat{q}\}\Big) + \Big(\sum_i h_{ii} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle\Big) + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} \\
&= \sum_{pq} f_{pq}\{\hat{p}^\dagger\hat{q}\} + \Big(\sum_i h_{ii} + \sum_{ij}\langle ij||ij\rangle\Big) - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} \\
&= \sum_{pq} f_{pq}\{\hat{p}^\dagger\hat{q}\} + \Big(\sum_i f_{ii} - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle\Big) + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} \\
&= \sum_{pq} f_{pq}\{\hat{p}^\dagger\hat{q}\} + E_{\text{HF}} + \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger\hat{q}^\dagger\hat{s}\hat{r}\} \tag{6}
\end{aligned}$$

In Møller–Plesset PT, the reference Hamiltonian is chosen to be the Fock operator:

$$\hat{H}^{(0)} = \hat{F} = \sum_{pq} f_{pq}\hat{p}^\dagger\hat{q} = \sum_{pq} f_{pq}\{\hat{p}^\dagger\hat{q}\} + \sum_i f_{ii} \tag{7}$$

The Fock matrix is defined as:

$$f_{pq} = h_{pq} + \sum_i\langle pi||qi\rangle \tag{8}$$

Hence, the electronic Hamiltonian could be partitioned into:

$$\hat{H}_{\text{elec}} = \hat{F} - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle + \hat{V} = \hat{H}^{(0)} + \hat{V} \tag{9}$$

where the perturbation:

$$\hat{V} = \hat{H}_{\text{elec}} - \hat{F} = \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\} - \frac{1}{2} \sum_{ij} \langle ij||ij \rangle \tag{10}$$

In summary: the zeroth-order Hamiltonian, perturbation, energy, and wavefunctions in spin-orbital basis:

$$\hat{H}^{(0)} = \sum_i^N f_{ii} + \sum_{pq}^N f_{pq}\{\hat{p}^\dagger \hat{q}\} \tag{11}$$

$$\hat{V} = \frac{1}{4} \sum_{pqrs} \langle pq||rs \rangle \{\hat{p}^\dagger \hat{q}^\dagger \hat{s} \hat{r}\} - \frac{1}{2} \sum_{ij} \langle ij||ij \rangle \tag{12}$$

$$|\Psi^{(0)}\rangle = |\Phi_{\text{HF}}\rangle = |\Phi_0\rangle \tag{13}$$

$$E^{(0)} = \langle \Phi_0 | \hat{H}^{(0)} | \Phi_0 \rangle = \sum_i^N f_{ii} = \sum_i \varepsilon_i \tag{14}$$

$$E^{(1)} = \langle \Phi_0 | \hat{V} | \Phi_0 \rangle = -\frac{1}{2} \sum_{ij} \langle ij||ij \rangle \tag{15}$$

From Rayleigh-Schrödinger PT, we know that the second order energy correction is:

$$E^{(2)} = \langle \Phi_0 | \hat{V} | \Psi^{(1)} \rangle \tag{16}$$

The first-order wavefunction is obtained by linear combination of zeroth-order wavefunctions.

$$|\Psi^{(1)}\rangle = \sum_{\eta \neq 0} \frac{\langle \Phi_\eta | \hat{V} | \Phi_0 \rangle}{E^{(0)} - E_\eta^{(0)}} |\Phi_\eta\rangle = \sum_i \sum_a T_i^a |\Phi_i^a\rangle + \sum_{i<j} \sum_{a<b} T_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \cdots \tag{17}$$

By Slater-Condon rule:

$$\langle \Phi_0 | \hat{V} | \Phi_I \rangle = 0 \tag{18}$$

for any determinant $|\Phi_I\rangle$ with more than double excitation. By Brillouin theorem:

$$\langle \Phi_0 | \hat{H} | \Phi_i^a \rangle = 0 \Leftrightarrow$$
$$\langle \Phi_0 | \hat{H}^{(0)} | \Phi_i^a \rangle + \langle \Phi_0 | \hat{V} | \Phi_i^a \rangle = 0 \Leftrightarrow$$
$$\langle \Phi_0 | \hat{V} | \Phi_i^a \rangle = 0 \tag{19}$$

Therefore, the only determinants contributing to second-order energy are the doubly excited ones. Considering the permutation symmetry of $|\Phi_{ij}^{ab}\rangle$, i.e. $|\Phi_{ij}^{ab}\rangle = -|\Phi_{ij}^{ba}\rangle = -|\Phi_{ji}^{ab}\rangle = |\Phi_{ji}^{ba}\rangle$, the first-order wavefunction could be written as:

$$|\Psi^{(1)}\rangle = \frac{1}{4} \sum_{ijab} T_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \tag{20}$$

To find the amplitude T_{ij}^{ab}, we solve the first-order RSPT equation by projecting $\langle \Phi_\eta | = \langle \Phi_{kl}^{cd}| \neq \langle \Phi_0 |$ onto it:

$$(\hat{H}^{(0)} - E^{(0)})|\Psi^{(1)}\rangle + (\hat{V} - E^{(1)})|\Phi_0\rangle = 0 \tag{21}$$
$$\langle \Phi_{kl}^{cd} | \hat{H}^{(0)} - E^{(0)} | \Psi^{(1)} \rangle + \langle \Phi_{kl}^{cd} | \hat{V} - E^{(1)} | \Phi_0 \rangle = 0 \Leftrightarrow$$
$$\frac{1}{4} \sum_{ijab} \langle \Phi_{kl}^{cd} | \hat{H}^{(0)} | \Phi_{ij}^{ab} \rangle T_{ij}^{ab} - \frac{1}{4} E^{(0)} \sum_{ijab} \langle \Phi_{kl}^{cd} | \Phi_{ij}^{ab} \rangle T_{ij}^{ab} + \langle \Phi_{kl}^{cd} | \hat{V} | \Phi_0 \rangle - E^{(1)} \langle \Phi_{kl}^{cd} | \Phi_0 \rangle = 0 \Leftrightarrow$$

$$\frac{1}{4} \sum_{ijab} E_{ijab}^{(0)} T_{ij}^{ab} \langle \Phi_{kl}^{cd} | \Phi_{ij}^{ab} \rangle - \frac{1}{4} E^{(0)} \sum_{ijab} T_{ij}^{ab} \langle \Phi_{kl}^{cd} | \Phi_{ij}^{ab} \rangle + \langle \Phi_{kl}^{cd} | \hat{V} | \Phi_0 \rangle = 0 \quad (22)$$

To work out the overlap integral:

$$|\Phi_{ij}^{ab}\rangle = \left(\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} + \sum_{\substack{\text{all possible} \\ \text{contractions}}} \{\overline{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}}\}\right)|\Phi_0\rangle \quad (23)$$

Noting that only fully contracted terms contribute to the vacuum expectation value:

$$\langle \Phi_{kl}^{cd} | \Phi_{ij}^{ab} \rangle = \sum_{\substack{\text{fully} \\ \text{contracted}}} \langle \Phi_0 | \{\hat{c}^\dagger \hat{d}^\dagger \hat{l}\hat{k}\} \{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} | \Phi_0 \rangle$$

$$= \delta_{ca}\delta_{db}\delta_{ki}\delta_{lj} - \delta_{ca}\delta_{db}\delta_{kj}\delta_{li} - \delta_{cb}\delta_{ad}\delta_{ki}\delta_{lj} + \delta_{cb}\delta_{ad}\delta_{kj}\delta_{li} \quad (24)$$

Therefore (exploiting the permutation symmetry $T_{ij}^{ab} = -T_{ji}^{ab} = -T_{ij}^{ba} = T_{ji}^{ba}$):

$$\sum_{ijab} T_{ij}^{ab} \langle \Phi_{kl}^{cd} | \Phi_{ij}^{ab} \rangle = T_{kl}^{cd} - T_{lk}^{cd} - T_{kl}^{dc} + T_{lk}^{dc} = 4 T_{kl}^{cd} \quad (25)$$

hence we obtain the amplitude as:

$$T_{kl}^{cd} = \frac{\langle \Phi_{kl}^{cd} | \hat{V} | \Phi_0 \rangle}{f_{kk} + f_{ll} - f_{cc} - f_{dd}} \quad (26)$$

and the second-order energy:

$$\begin{aligned} E^{(2)} &= \langle \Phi_0 | \hat{V} | \Psi^{(1)} \rangle \\ &= \frac{1}{4} \sum_{ijab} \langle \Phi_0 | \hat{V} | \Phi_{ij}^{ab} \rangle T_{ij}^{ab} \\ &= \frac{1}{4} \sum_{ijab} \frac{\langle \Phi_0 | \hat{V} | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | \hat{V} | \Phi_0 \rangle}{f_{ii} + f_{jj} - f_{aa} - f_{bb}} \\ &= \frac{1}{4} \sum_{ijab} \frac{\langle ij||ab\rangle \langle ab||ij\rangle}{f_{ii} + f_{jj} - f_{aa} - f_{bb}} \end{aligned} \quad (27)$$

note that the $-\frac{1}{2}\sum_{ij}\langle ij||ij\rangle$ part in $\hat{V}$ does not contribute to the second-order energy, since $\langle \Phi_0 | \Phi_{ij}^{ab} \rangle = 0$.

The total energy up to MP2-level correction is:

$$\begin{aligned} E_{\text{MP2}} &= E^{(0)} + E^{(1)} + E^{(2)} \\ &= \sum_i h_{ii} + \sum_{ij} \langle ij||ij\rangle - \frac{1}{2}\sum_{ij}\langle ij||ij\rangle + E^{(2)} \\ &= \underbrace{\sum_i h_{ii} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle}_{E_{\text{HF}} = E^{(0)} + E^{(1)}} + \frac{1}{4}\sum_{ijab} \frac{\langle ij||ab\rangle \langle ab||ij\rangle}{f_{ii} + f_{jj} - f_{aa} - f_{bb}} \end{aligned} \quad (28)$$

2 Spin-Adapted-Orbital Formalism

$$\hat{E}_q^p = \sum_\sigma \hat{p}_\sigma^\dagger \hat{q}_\sigma \tag{29}$$

$$\hat{e}_{rs}^{pq} = \sum_{\sigma\tau} \hat{p}_\sigma^\dagger \hat{q}_\tau^\dagger \hat{s}_\tau \hat{r}_\sigma \tag{30}$$

Noting that $[\hat{p}^\dagger, \hat{q}]_+ = \delta_{pq}$, we can get the relationship between one- and two-body operators:

$$
\begin{aligned}
\hat{e}_{qs}^{pr} &= \sum_{\sigma\tau} \hat{p}_\sigma^\dagger \hat{r}_\tau^\dagger \hat{s}_\tau \hat{q}_\sigma \\
&= -\sum_{\sigma\tau} \hat{p}_\sigma^\dagger \hat{r}_\tau^\dagger \hat{q}_\sigma \hat{s}_\tau \\
&= -\sum_{\sigma\tau} \hat{p}_\sigma^\dagger (\delta_{rq}\delta_{\sigma\tau} - \hat{q}_\sigma \hat{r}_\tau^\dagger) \hat{s}_\tau \\
&= \sum_{\sigma\tau} \hat{p}_\sigma^\dagger \hat{q}_\sigma \hat{r}_\tau^\dagger \hat{s}_\tau - \sum_{\sigma\tau} \hat{p}_\sigma^\dagger \hat{s}_\tau \delta_{rq}\delta_{\sigma\tau} \\
&= \hat{E}_q^p \hat{E}_s^r - \delta_{rq} \sum_\sigma \hat{p}_\sigma^\dagger \hat{s}_\sigma \\
&= \hat{E}_q^p \hat{E}_s^r - \delta_{rq} \hat{E}_s^p
\end{aligned}
\tag{31}
$$

Consider the permutation symmetry of the two-body operator:

$$
\begin{aligned}
\hat{e}_{sq}^{rp} &= \sum_{\sigma\tau} \hat{r}_\sigma^\dagger \hat{p}_\tau^\dagger \hat{q}_\tau \hat{s}_\sigma \\
&= -\sum_{\sigma\tau} \hat{p}_\tau^\dagger \hat{r}_\sigma^\dagger \hat{q}_\tau \hat{s}_\sigma \\
&= \sum_{\sigma\tau} \hat{p}_\tau^\dagger \hat{r}_\sigma^\dagger \hat{s}_\sigma \hat{q}_\tau \\
&= \hat{e}_{qs}^{pr}
\end{aligned}
\tag{32}
$$

we can evaluate the commutation relation between one-body operators:

$$
\begin{aligned}
[\hat{E}_q^p, \hat{E}_s^r] &= \hat{E}_q^p \hat{E}_s^r - \hat{E}_s^r \hat{E}_q^p \\
&= e_{qs}^{pr} + \delta_{rq}\hat{E}_s^p - (\hat{e}_{sq}^{rp} + \delta_{ps}\hat{E}_q^r) \\
&= \delta_{rq}\hat{E}_s^p - \delta_{ps}\hat{E}_q^r
\end{aligned}
\tag{33}
$$

Using this relation, we can evaluate the overlap integral of doubly-excited determinants:

$$
\begin{aligned}
\langle \Phi_{ij}^{ab} | \Phi_{kl}^{cd} \rangle &= \delta_{ac}\delta_{bd}\langle \Phi_0 | \hat{e}_{kl}^{ij} | \Phi_0 \rangle + \delta_{ad}\delta_{bc}\langle \Phi_0 | \hat{e}_{lk}^{ij} | \Phi_0 \rangle \\
&= \delta_{ad}\delta_{bc}(4\delta_{jk}\delta_{il} - 2\delta_{ik}\delta_{jl}) + \delta_{ac}\delta_{bd}(4\delta_{jl}\delta_{ik} - 2\delta_{il}\delta_{jk})
\end{aligned}
\tag{34}
$$

3 Spin-Adapted-Contravariant-Configuration Formalism

The Hamiltonian in spin-adapted form:

$$\hat{H}_{\text{elec}} = \sum_{pq} h_{pq} \hat{E}^p_q + \frac{1}{2} \sum_{pqrs} \langle pq|rs \rangle \hat{e}^{pq}_{rs} \tag{35}$$

$$\hat{H}_{\text{elec}} = \sum_{pq} h_{pq} \hat{E}^p_q + \frac{1}{2} \sum_{pqrs} \langle pq|rs \rangle (\hat{E}^p_r \hat{E}^q_s - \delta_{qr} \hat{E}^p_s)$$
$$= \sum_{pq} h_{pq} \hat{E}^p_q + \frac{1}{2} \sum_{pqs} \langle pq|sq \rangle \hat{E}^p_s + \frac{1}{2} \sum_{pqrs} \langle pq|rs \rangle \hat{E}^p_r \hat{E}^q_s \tag{36}$$

The contravariant configurations:

$$|\tilde{\Phi}^a_i\rangle = \frac{1}{2}|\Phi^a_i\rangle = \frac{1}{2}\hat{E}^a_i|\Phi_0\rangle \tag{37}$$

$$|\tilde{\Phi}^{ab}_{ij}\rangle = \frac{1}{6}(2|\Phi^{ab}_{ij}\rangle + |\Phi^{ab}_{ji}\rangle) = \frac{1}{6}(2\hat{E}^a_i \hat{E}^b_j + \hat{E}^a_j \hat{E}^b_i)|\Phi_0\rangle \tag{38}$$

Now:

$$\langle \tilde{\Phi}^{ab}_{ij}|\Phi^{cd}_{kl}\rangle = \frac{1}{3}\langle \Phi^{ab}_{ij}|\Phi^{cd}_{kl}\rangle + \frac{1}{6}\langle \Phi^{ab}_{ji}|\Phi^{cd}_{kl}\rangle$$
$$= \frac{1}{3}(\delta_{ad}\delta_{bc}(4\delta_{jk}\delta_{il} - 2\color{red}{\delta_{ik}\delta_{jl}}\color{black}) + \delta_{ac}\delta_{bd}(4\delta_{jl}\delta_{ik} - 2\color{blue}{\delta_{jk}\delta_{il}}\color{black}))$$
$$\quad + \frac{1}{6}(\delta_{ad}\delta_{bc}(4\color{red}{\delta_{ik}\delta_{jl}}\color{black} - 2\delta_{jk}\delta_{il}) + \delta_{ac}\delta_{bd}(4\color{blue}{\delta_{jl}\delta_{jk}}\color{black} - 2\delta_{ik}\delta_{jl}))$$
$$= \delta_{ad}\delta_{bc}\delta_{jk}\delta_{il} + \delta_{ac}\delta_{bd}\delta_{jl}\delta_{ik} \tag{39}$$

*Derivation

Spin-orbital Formalism

Some expansions using Wick's theorem:
Expanding the electronic Hamiltonian using Wick's theorem:

$$\hat{p}^\dagger \hat{q} = \{\hat{p}^\dagger \hat{q}\} + \{\overline{\hat{p}^\dagger \hat{q}}\} = \{\hat{p}^\dagger \hat{q}\} + \delta_{pq}\delta_{pi} \tag{40}$$

$$
\begin{aligned}
\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r} =& \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} + \{\overline{\hat{p}^\dagger \hat{q}^\dagger \hat{s}}\hat{r}\} + \{\overline{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}}\} + \{\hat{p}^\dagger \overline{\hat{q}^\dagger \hat{s}}\hat{r}\} + \{\hat{p}^\dagger \overline{\hat{q}^\dagger \hat{s}\hat{r}}\} + \{\overline{\hat{p}^\dagger \hat{q}^\dagger}\,\overline{\hat{s}\hat{r}}\} + \{\overline{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}}\} \\
=& \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} - \delta_{ps}\delta_{pi}\{\hat{q}^\dagger \hat{r}\} + \delta_{pr}\delta_{pi}\{\hat{q}^\dagger \hat{s}\} + \delta_{qs}\delta_{qi}\{\hat{p}^\dagger \hat{r}\} - \delta_{qr}\delta_{qi}\{\hat{p}^\dagger \hat{s}\} \\
& + \delta_{pr}\delta_{pi}\delta_{qs}\delta_{qj} - \delta_{ps}\delta_{pi}\delta_{qr}\delta_{qj} \tag{41}
\end{aligned}
$$

hence:

$$
\begin{aligned}
\sum_{pq} h_{pq}\hat{p}^\dagger \hat{q} &= \sum_{pq} h_{pq}\{\hat{p}^\dagger \hat{q}\} + \sum_{pq} h_{pq}\delta_{pq}\delta_{pi} \\
&= \sum_{pq} h_{pq}\{\hat{p}^\dagger \hat{q}\} + \sum_i h_{ii} \tag{42}
\end{aligned}
$$

$$
\begin{aligned}
\frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r} =& \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} - \frac{1}{4}\sum_{iqr}\langle iq||ri\rangle\{\hat{q}^\dagger \hat{r}\} + \frac{1}{4}\sum_{iqs}\langle iq||is\rangle\{\hat{q}^\dagger \hat{s}\} \\
& + \frac{1}{4}\sum_{ipr}\langle pi||ri\rangle\{\hat{p}^\dagger \hat{r}\} - \frac{1}{4}\sum_{ips}\langle pi||is\rangle\{\hat{p}^\dagger \hat{s}\} \\
& + \frac{1}{4}\sum_{ij}\langle ij||ijab\rangle - \frac{1}{4}\sum_{ij}\langle ij||ji\rangle \\
=& \frac{1}{4}\sum_{pqrs}\langle pq||rs\rangle\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\} + \sum_{pqi}\langle pi||qi\rangle\{\hat{p}^\dagger \hat{q}\} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle \tag{43}
\end{aligned}
$$

The perturbation integral:

$$
\begin{aligned}
\langle \Phi_0|\hat{V}|\Phi_{ij}^{ab}\rangle =& \frac{1}{4}\sum_{pqrs}\langle \Phi_0|\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\}\{\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\}|\Phi_0\rangle\langle pq||rs\rangle \\
=& \frac{1}{4}\sum_{pqrs}\langle \Phi_0|\Big(\{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} \\
& + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\} + \{\hat{p}^\dagger \hat{q}^\dagger \hat{s}\hat{r}\hat{a}^\dagger \hat{b}^\dagger \hat{j}\hat{i}\}\Big)|\Phi_0\rangle\langle pq||rs\rangle \\
=& \frac{1}{4}\sum_{pqrs}(\delta_{pi}\delta_{qj}\delta_{sb}\delta_{ra} - \delta_{pj}\delta_{qi}\delta_{sb}\delta_{ra} - \delta_{pi}\delta_{qj}\delta_{sa}\delta_{rb} + \delta_{pj}\delta_{qi}\delta_{sa}\delta_{rb})\langle pq||rs\rangle \\
=& \frac{1}{4}(\langle ij||ab\rangle - \langle ji||ab\rangle - \langle ij||ba\rangle + \langle ji||ba\rangle) \\
=& \langle ij||ab\rangle \tag{44}
\end{aligned}
$$

Spin-Adapted Formalism

(Blue indicates the operator pairs being swapped)

$$
\begin{aligned}
\langle\Phi_{ij}^{ab}|\Phi_{kl}^{cd}\rangle =&\langle\Phi_0|\hat{E}_b^j\hat{E}_a^i\hat{E}_k^c\hat{E}_l^d|\Phi_0\rangle\\
=&\langle\Phi_0|\hat{E}_b^j\hat{E}_k^c\hat{E}_a^i\hat{E}_l^d|\Phi_0\rangle + \delta_{ac}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^i\hat{E}_l^d|\Phi_0\rangle - \delta_{ik}\langle\Phi_0|\hat{E}_b^j\hat{E}_a^c\hat{E}_l^d|\Phi_0\rangle\\
=&\langle\Phi_0|\hat{E}_b^j\hat{E}_k^c\hat{E}_l^d\hat{E}_a^i|\Phi_0\rangle + \delta_{ad}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^c\hat{E}_l^i|\Phi_0\rangle - \delta_{il}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^c\hat{E}_a^d|\Phi_0\rangle\\
&+ \delta_{ac}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^i\hat{E}_l^d|\Phi_0\rangle - \delta_{ik}\langle\Phi_0|\hat{E}_b^j\hat{E}_a^c\hat{E}_l^d|\Phi_0\rangle\\
=&\delta_{ad}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^c\hat{E}_l^i|\Phi_0\rangle - \delta_{il}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^c\hat{E}_a^d|\Phi_0\rangle\\
&+ \delta_{ac}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^i\hat{E}_l^d|\Phi_0\rangle - \delta_{ik}\langle\Phi_0|\hat{E}_b^j\hat{E}_a^c\hat{E}_l^d|\Phi_0\rangle
\end{aligned}
\tag{45}
$$

Evaluating term by term (noting that $\hat{E}_b^a|\Phi_0\rangle = 0$):

$$
\begin{aligned}
\langle\Phi_0|\hat{E}_b^j\hat{E}_k^c\hat{E}_l^i|\Phi_0\rangle =&\cancel{\langle\Phi_0|\hat{E}_k^c\hat{E}_b^j\hat{E}_l^i|\Phi_0\rangle} + \delta_{bc}\langle\Phi_0|\hat{E}_k^j\hat{E}_l^i|\Phi_0\rangle - \delta_{jk}\langle\Phi_0|\hat{E}_b^c\hat{E}_l^i|\Phi_0\rangle\\
=&\delta_{bc}\langle\Phi_0|\hat{E}_k^j\hat{E}_l^i|\Phi_0\rangle - \delta_{jk}\cancel{\langle\Phi_0|\hat{E}_b^c\hat{E}_l^i|\Phi_0\rangle}
\end{aligned}
\tag{46}
$$

$$
\langle\Phi_0|\hat{E}_b^j\hat{E}_k^c\cancel{\hat{E}_a^d|\Phi_0\rangle} =0
\tag{47}
$$

$$
\begin{aligned}
\langle\Phi_0|\hat{E}_b^j\hat{E}_k^i\hat{E}_l^d|\Phi_0\rangle =&\langle\Phi_0|\hat{E}_b^j\hat{E}_l^d\hat{E}_k^i|\Phi_0\rangle + \cancel{\delta_{dk}}\langle\Phi_0|\hat{E}_b^j\hat{E}_l^i|\Phi_0\rangle - \delta_{il}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^d|\Phi_0\rangle\\
=&\cancel{\langle\Phi_0|\hat{E}_l^d\hat{E}_b^j\hat{E}_k^i|\Phi_0\rangle} + \delta_{bd}\langle\Phi_0|\hat{E}_l^j\hat{E}_k^i|\Phi_0\rangle - \delta_{jl}\langle\Phi_0|\hat{E}_b^d\hat{E}_k^i|\Phi_0\rangle\\
&- \delta_{il}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^d|\Phi_0\rangle\\
=&\delta_{bd}\langle\Phi_0|\hat{E}_l^j\hat{E}_k^i|\Phi_0\rangle - \delta_{jl}\cancel{\langle\Phi_0|\hat{E}_b^d\hat{E}_k^i|\Phi_0\rangle} - \delta_{il}\langle\Phi_0|\hat{E}_b^j\hat{E}_k^d|\Phi_0\rangle
\end{aligned}
\tag{48}
$$

$$
\begin{aligned}
\langle\Phi_0|\hat{E}_b^j\hat{E}_a^c\hat{E}_l^d|\Phi_0\rangle =&\langle\Phi_0|\hat{E}_b^j\hat{E}_l^d\cancel{\hat{E}_a^c|\Phi_0\rangle} + \delta_{ad}\langle\Phi_0|\hat{E}_b^j\hat{E}_l^c|\Phi_0\rangle - \cancel{\delta_{cl}}\langle\Phi_0|\hat{E}_b^j\hat{E}_a^d|\Phi_0\rangle\\
=&\delta_{ad}\langle\Phi_0|\hat{E}_b^j\hat{E}_l^c|\Phi_0\rangle
\end{aligned}
\tag{49}
$$

The violet terms (using $\hat{E}_j^i|\Phi_0\rangle = (\hat{i}_\alpha^\dagger\hat{j}_\alpha + \hat{i}_\beta^\dagger\hat{j}_\beta)|\Phi_0\rangle = 2\delta_{ij}|\Phi_0\rangle$):

$$
\begin{aligned}
\langle\Phi_0|\hat{E}_b^j\hat{E}_l^c|\Phi_0\rangle =&\langle\Phi_0|\hat{E}_l^c\cancel{\hat{E}_b^j|\Phi_0\rangle} + \delta_{bc}\langle\Phi_0|\hat{E}_l^j|\Phi_0\rangle - \delta_{jl}\langle\Phi_0|\cancel{\hat{E}_b^c|\Phi_0\rangle}\\
=&2\delta_{bc}\delta_{jl}
\end{aligned}
\tag{50}
$$

$$
\langle\Phi_0|\hat{E}_b^j\hat{E}_k^d|\Phi_0\rangle =2\delta_{bd}\delta_{jk}
\tag{51}
$$

Putting them together :

$$
\begin{aligned}
\langle\Phi_{ij}^{ab}|\Phi_{kl}^{cd}\rangle =&\delta_{ad}\delta_{bc}\langle\Phi_0|\hat{E}_k^j\hat{E}_l^i|\Phi_0\rangle + \delta_{ac}\delta_{bd}\langle\Phi_0|\hat{E}_l^j\hat{E}_k^i|\Phi_0\rangle\\
&- 2\delta_{ac}\delta_{il}\delta_{bd}\delta_{jk} - 2\delta_{ik}\delta_{ad}\delta_{bc}\delta_{jl}\\
=&4\delta_{ad}\delta_{bc}\delta_{jk}\delta_{il} + 4\delta_{ac}\delta_{bd}\delta_{jl}\delta_{ik} - 2\delta_{ac}\delta_{bd}\delta_{il}\delta_{jk} - 2\delta_{ad}\delta_{bc}\delta_{ik}\delta_{jl}\\
=&\delta_{ad}\delta_{bc}(4\delta_{jk}\delta_{il} - 2\delta_{ik}\delta_{jl}) + \delta_{ac}\delta_{bd}(4\delta_{jl}\delta_{ik} - 2\delta_{il}\delta_{jk})
\end{aligned}
\tag{52}
$$