Evaluating CI matrix elements up to double excitations

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1 Introduction

This small document attempts to describe the (manual) derivation of the CI matrix elements using two different approaches: the Slater-Condon rules and the second quantization. Since the derivation procedure is basically the same for both the determinantal and the configuration state bases. Here we restrict ourselves to the generation of CI matrix elements in the determinantal basis and focus merely on determinants up to double excitations. The matrix elements will be expressed in terms of both single-bar and double-bar integrals.

We adopt the notation used in Szabo and Ostlund, *Modern Quantum Chemistry*. Below is the list of symbols that will be used here.

N	number of electrons
a, b, c, d	occupied orbital indices
r, s, t, u	unoccupied orbital indices
i, j, k, l	all orbital indices
$\|\Psi_0\rangle$	Hartree-Fock (HF) Slater determinant
$\|\Psi_a^r\rangle$	singly excited determinant based on the reference Ψ_0 state, by replacing orbital a with r
$\|\Psi_{ab}^{rs}\rangle$	doubly excited determinant based on the reference Ψ_0 state, by replacing orbital a with r and replacing b with s, to avoid double counting, we have the constraint: $a < b, r < s$
$\hat{H}$	the exact nonrelativistic Hamiltonian operator
$\hat{h}$	the one-electron operator
$\hat{f}$	the Fock operator
$\|i\rangle$	general spin orbital or spin orbital with alpha spin
$\|\bar{i}\rangle$	spin orbital with beta spin
$\|i)$	spatial orbital

$\langle ij\|kl\rangle$	the two-electron integral in physicists' notation, where i, j, k, l are **spin** orbitals
$\langle ij\|\|kl\rangle$	the anti-symmetrized two-electron integral, equal to $\langle ij\|kl\rangle - \langle ij\|lk\rangle$
$(ij\|kl)$	the two-electron integral in chemists' notation, where i, j, k, l are **spatial** orbitals: $(ij\|kl) = \int \phi_i^*(\mathbf{r}_1)\phi_j(\mathbf{r}_1)\mathbf{r}_{12}^{-1}\phi_k^*(\mathbf{r}_2)\phi_l(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$
J_{ij}	the *coulomb* integral, equal to $(ii\|jj)$
K_{ij}	the *exchange* integral, equal to $(ij\|ji)$
$a_i^\dagger$	second-quantized creation operator for orbital i
a_i	second-quantized annihilationn operator for orbital i

Some useful expressions:

1. Ground state energy E_0

$$\begin{aligned} E_0 &= \langle\Psi_0|\hat{H}|\Psi_0\rangle \\ &= \sum_a^N \langle a|h|a\rangle + \frac{1}{2}\sum_{ab}^N \langle ab||ab\rangle \qquad \text{(in spin orbitals)} \quad (1) \\ &= 2\sum_a^{N/2}(a|h|a) + \sum_{ab}^{N/2} 2J_{ab} - K_{ab} \qquad \text{(in spatial orbitals)} \quad (2) \end{aligned}$$

2. Orbital energies ε_i

$$\begin{aligned} \varepsilon_i &= \langle i|h|i\rangle + \sum_j^N \langle ij||ij\rangle \qquad \text{(in spin orbitals)} \quad (3) \\ &= (i|h|i) + \sum_j^{N/2} 2J_{ij} - K_{ij} \qquad \text{(in spatial orbitals)} \quad (4) \end{aligned}$$

3. For *converged* HF spin orbitals,

$$\langle i|\hat{f}|j\rangle = \langle i|h|j\rangle + \sum_k^N \langle ik||jk\rangle = \delta_{ij}\varepsilon_i$$

2 Evaluating CI matrix elements using Slater-Condon rules

The Slater-Condon rules express the matrix elements of the one- and two-electron operators between two Slater determinants. Tables 2.3 and 2.4 in Szabo and Ostlund summerize the

results. Since the exact nonrelativistic Hamiltonian operator is simply a combination of one- and two-electron operators, we can directly apply the Slater-Condon rules to the generation of CI matrix elements. Here we only consider elements involving determinants up to double excitations, which will include the following terms:
(1) HF-HF ($\langle\Psi_0|\hat{H}|\Psi_0\rangle$),
(2) HF-Single ($\langle\Psi_0|\hat{H}|\Psi_a^r\rangle$),
(3) Single-Single ($\langle\Psi_a^r|\hat{H}|\Psi_b^s\rangle$),
(4) HF-Double ($\langle\Psi_0|\hat{H}|\Psi_{ab}^{rs}\rangle$),
(5) Single-Double ($\langle\Psi_a^r|\hat{H}|\Psi_{bc}^{st}\rangle$),
(6) Double-Double ($\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{cd}^{tu}\rangle$)

2.1 HF-HF ($\langle\Psi_0|\hat{H}|\Psi_0\rangle$)

The matrix element between the two HF ground state determinants can be derived straightforwardly using the Slater-Condon rules (Case 1 in Tables 2.3 and 2.4 in Szabo and Ostlund). The expressions in spin and spatial orbital bases are given above in Eq. (1) and Eq. (2).

2.2 HF-Single ($\langle\Psi_0|\hat{H}|\Psi_a^r\rangle$)

The matrix element between HF ground state Ψ_0 and an arbitrary singly excited determinant Ψ_a^r can be derived following Case 2 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$\begin{aligned}\langle\Psi_0|\hat{H}|\Psi_a^r\rangle &= \langle\Psi_0|\mathcal{O}_1|\Psi_a^r\rangle + \langle\Psi_0|\mathcal{O}_2|\Psi_a^r\rangle \\ &= \langle a|h|r\rangle + \sum_i^N \langle ai||ri\rangle\end{aligned}$$

Recognizing that the last expression is actually equal to the matrix element of the Fock operator, and the off-diagonal elements of the Fock operator *at convergence* is zero, we have

$$\boxed{\langle\Psi_0|\hat{H}|\Psi_a^r\rangle = \langle a|\hat{f}|r\rangle = 0}$$

This is essentially the Brillouin's Theorem.

2.3 Single-Single ($\langle\Psi_a^r|\hat{H}|\Psi_b^s\rangle$)

Now we get to the more complicated case: the matrix element between two arbitrary singly excited determinants Ψ_a^r and Ψ_b^s, where the two determinants are not necessarily the same. In order to apply the Slater-Condon rules to this case, we need to consider ALL possible

situations, that is: (1) $a = b, r = s$, (2) $a = b, r \neq s$, (3) $a \neq b, r = s$, and (4) $a \neq b, r \neq s$. Let's look at them one by one:

(1) If $a = b, r = s$, the matrix element becomes $\langle \Psi_a^r | \hat{H} | \Psi_a^r \rangle$. We apply Case 1 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$\begin{aligned}\langle \Psi_a^r | \hat{H} | \Psi_a^r \rangle = &\sum_i^N \langle i|h|i\rangle - \langle a|h|a\rangle + \langle r|h|r\rangle \\ &+ \frac{1}{2}\sum_i^N \sum_j^N \langle ij||ij\rangle - \sum_i^N \langle ai||ai\rangle + \sum_i^N \langle ri||ri\rangle - \langle ra||ra\rangle\end{aligned}$$

Applying Eq. (1) and Eq. (3), we have,

$$\langle \Psi_a^r | \hat{H} | \Psi_a^r \rangle = E_0 - \varepsilon_a + \varepsilon_r - \langle ra||ra\rangle$$

(2) If $a = b, r \neq s$, the matrix element is $\langle \Psi_a^r | \hat{H} | \Psi_a^s \rangle$. We apply Case 2 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$\begin{aligned}\langle \Psi_a^r | \hat{H} | \Psi_a^s \rangle &= \langle r|h|s\rangle + \sum_j^N \langle ri||si\rangle - \langle ra||sa\rangle \\ &= \langle r|\hat{f}|s\rangle - \langle ra||sa\rangle \\ &= -\langle ra||sa\rangle\end{aligned}$$

(3) If $a \neq b, r = s$, the matrix element is $\langle \Psi_a^r | \hat{H} | \Psi_b^r \rangle$. Similar to situation (2), we can get

$$\begin{aligned}\langle \Psi_a^r | \hat{H} | \Psi_b^r \rangle &= -\langle a|h|b\rangle - \sum_j^N \langle ai||bi\rangle - \langle ar||br\rangle \\ &= \langle a|\hat{f}|b\rangle - \langle rb||ra\rangle \\ &= -\langle rb||ra\rangle\end{aligned}$$

(4) If $a \neq b, r \neq s$, the matrix element becomes $\langle \Psi_a^r | \hat{H} | \Psi_b^s \rangle$. We apply Case 3 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$\begin{aligned}\langle \Psi_a^r | \hat{H} | \Psi_b^s \rangle &= \langle rb||as\rangle \\ &= -\langle rb||sa\rangle\end{aligned}$$

Grouping all the above four situations together, we can write a compact expression for a

general matrix element $\langle \Psi_a^r | \hat{H} | \Psi_b^s \rangle$:

$$\boxed{\langle \Psi_a^r | \hat{H} | \Psi_b^s \rangle = \delta_{ab}\delta_{rs}(E_0 - \varepsilon_a + \varepsilon_r) - \langle rb||sa \rangle}$$

2.4 HF-Double ($\langle \Psi_0 | \hat{H} | \Psi_{ab}^{rs} \rangle$)

The matrix elements between reference HF determinant and doubly excited determinants can be easily evaluated applying Case 3 in Tables 2.3 and 2.4, or simply Table 2.6 in Szabo and Ostlund:

$$\boxed{\langle \Psi_0 | \hat{H} | \Psi_{ab}^{rs} \rangle = \langle ab||rs \rangle}$$

2.5 Single-Double ($\langle \Psi_a^r | \hat{H} | \Psi_{bc}^{st} \rangle$)

To apply the Slater-Condon rules to a general matrix element between an arbitrary single Ψ_a^r and arbitrary double Ψ_{bc}^{st}, we need to consider ALL possible situations as following:
(1) $a \neq b, a \neq c, r \neq s, r \neq t$;
(2) $a = b, r \neq s, r \neq t$;
(3) $a = c, r \neq s, r \neq t$;
(4) $a \neq b, a \neq c, r = s$;
(5) $a \neq b, a \neq c, r = t$;
(6) $a = b, r = s$;
(7) $a = b, r = t$;
(8) $a = c, r = s$;
(9) $a = c, r = t$;
Let's examine them one by one.
(1) If $a \neq b, a \neq c, r \neq s, r \neq t$, the two determinants Ψ_a^r and Ψ_{bc}^{st} will differ by three spin orbitals. According Slater-Condon rules, in this case the matrix element $\langle \Psi_a^r | \hat{H} | \Psi_{bc}^{st} \rangle$ will be zero:

$$\langle \Psi_a^r | \hat{H} | \Psi_{bc}^{st} \rangle = 0$$

(2) If $a = b, r \neq s, r \neq t$, the matrix element becomes $\langle \Psi_a^r | \hat{H} | \Psi_{ac}^{st} \rangle$, this is Case 3 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$|\Psi_a^r\rangle = |\cdots rc \cdots\rangle$$
$$|\Psi_{ac}^{st}\rangle = |\cdots st \cdots\rangle$$

Thus we have,

$$\langle \Psi_a^r | \hat{H} | \Psi_{ac}^{st} \rangle = \langle rc || st \rangle$$

(3) If $a = c, r \neq s, r \neq t$, the matrix element becomes $\langle \Psi_a^r | \hat{H} | \Psi_{ba}^{st} \rangle$. Then,

$$|\Psi_a^r\rangle = |\cdots rb \cdots\rangle$$
$$|\Psi_{ba}^{st}\rangle = |\cdots ts \cdots\rangle$$

$$\langle \Psi_a^r | \hat{H} | \Psi_{ba}^{st} \rangle = \langle rb || ts \rangle$$

(4) If $a \neq b, a \neq c, r = s$, then we have $\langle \Psi_a^r | \hat{H} | \Psi_{bc}^{rt} \rangle$. The two determinants still differ by two spin-orbitals:

$$|\Psi_a^r\rangle = |\cdots rbc \cdots\rangle$$
$$|\Psi_{ba}^{st}\rangle = |\cdots art \cdots\rangle = -|\cdots rat \cdots\rangle$$

Therefore,

$$\langle \Psi_a^r | \hat{H} | \Psi_{bc}^{rt} \rangle = -\langle bc || at \rangle$$

(5) Similarly, for $a \neq b, a \neq c, r = t$,

$$\langle \Psi_a^r | \hat{H} | \Psi_{bc}^{sr} \rangle = -\langle bc || sa \rangle$$

(6) If $a = b, r = s$, the matrix element is $\langle \Psi_a^r | \hat{H} | \Psi_{ac}^{rt} \rangle$. We have

$$|\Psi_a^r\rangle = |\cdots rc \cdots\rangle$$
$$|\Psi_{ba}^{st}\rangle = |\cdots rt \cdots\rangle$$

Applying Case 2 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$\begin{aligned}
\langle \Psi_a^r | \hat{H} | \Psi_{ac}^{rt} \rangle &= \langle c | h | t \rangle + \sum_i^N \langle ci || ti \rangle - \langle ca || ta \rangle + \langle cr || tr \rangle \\
&= \cancelto{0}{\langle c | \hat{f} | t \rangle} - \langle ca || ta \rangle + \langle cr || tr \rangle \\
&= -\langle ca || ta \rangle + \langle cr || tr \rangle
\end{aligned}$$

Similarly for Situations (7), (8), (9), we have

(7) If $a = b, r = t$,

$$\langle \Psi_a^r | \hat{H} | \Psi_{ac}^{sr} \rangle = \langle ca || sa \rangle - \langle cr || sr \rangle$$

(8) If $a = c, r = s$,

$$\langle \Psi_a^r | \hat{H} | \Psi_{ba}^{rt} \rangle = \langle ba || ta \rangle - \langle br || tr \rangle$$

(9) If $a = c, r = t$,

$$\langle \Psi_a^r | \hat{H} | \Psi_{ba}^{sr} \rangle = -\langle ba || sa \rangle + \langle br || sr \rangle$$

We can write a compact expression for a general Single-Double matrix element:

$$\boxed{\langle \Psi_a^r | \hat{H} | \Psi_{bc}^{st} \rangle = \delta_{ab} \langle rc || st \rangle - \delta_{ac} \langle rb || st \rangle + \delta_{rs} \langle bc || ta \rangle - \delta_{rt} \langle bc || sa \rangle}$$

2.6 Double-Double ($\langle \Psi_{ab}^{rs} | \hat{H} | \Psi_{cd}^{tu} \rangle$)

Now we reach the point where we have to evaulate the matrix elements between double and double. Again to apply the Slater-Condon rules to this case, we need to consider ALL possible situations. However, there are 36 combinations! Here we will not evaluate each combination individually, instead we only examine a subset of these combinations. Specifically we look at the following subset of combinations:

$$a = c, b = d, \begin{cases} r = t, s = u; \\ r = t, s \neq u; \\ r \neq t, s = u; \\ r \neq t, s \neq u \end{cases}$$

(1) If $a = c, b = d, r = t, s = u$, the matrix element becomes $\langle \Psi_{ab}^{rs} | \hat{H} | \Psi_{ab}^{rs} \rangle$. Applying Case 1 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$\begin{aligned} \langle \Psi_{ab}^{rs} | \hat{H} | \Psi_{ab}^{rs} \rangle = & \sum_i^N \langle i|h|i \rangle - \langle a|h|a \rangle - \langle b|h|b \rangle + \langle r|h|r \rangle + \langle s|h|s \rangle \\ & + \frac{1}{2} \sum_{ij}^N \langle ij || ij \rangle - \sum_i^N \langle ai || ai \rangle - \sum_i^N \langle bi || bi \rangle + \langle ab || ab \rangle \\ & + \sum_i^N \langle ri || ri \rangle + \sum_i^N \langle si || si \rangle - \langle ra || ra \rangle - \langle rb || rb \rangle \\ & - \langle sa || sa \rangle - \langle sb || sb \rangle + \langle rs || rs \rangle \end{aligned}$$

Using Eq. (1) and Eq. (3), we can simplify the above expression:

$$\begin{aligned}\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{ab}^{rs}\rangle = E_0 - \varepsilon_a - \varepsilon_b + \varepsilon_r + \varepsilon_s + \langle ab||ab\rangle + \langle rs||rs\rangle \\ - \langle ra||ra\rangle - \langle rb||rb\rangle - \langle sa||sa\rangle - \langle sb||sb\rangle\end{aligned}$$

(2) If $a = c, b = d, r = t, s \neq u$, the matrix element becomes $\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{ab}^{ru}\rangle$. We have

$$\begin{aligned}|\Psi_{ab}^{rs}\rangle &= |\cdots rs\cdots\rangle \\ |\Psi_{ab}^{ru}\rangle &= |\cdots ru\cdots\rangle\end{aligned}$$

and applying Case 2 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$\begin{aligned}\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{ab}^{ru}\rangle &= \langle s|h|u\rangle + \sum_i^N \langle si||ui\rangle - \langle sa||ua\rangle - \langle sb||ub\rangle + \langle sr||ur\rangle \\ &= \cancelto{0}{\langle s|\hat{f}|u\rangle} - \langle sa||ua\rangle - \langle sb||ub\rangle + \langle sr||ur\rangle \\ &= -\langle sa||ua\rangle - \langle sb||ub\rangle + \langle sr||ur\rangle\end{aligned}$$

(3) Similarly, for $a = c, b = d, r \neq t, s = u$, the matrix element $\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{ab}^{ts}\rangle$ will be expressed as

$$\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{ab}^{ts}\rangle = -\langle ra||ta\rangle - \langle rb||tb\rangle + \langle rs||ts\rangle$$

(4) If $a = c, b = d, r \neq t, s \neq u$, the matrix element is $\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{ab}^{tu}\rangle$. We have

$$\begin{aligned}|\Psi_{ab}^{rs}\rangle &= |\cdots rs\cdots\rangle \\ |\Psi_{ab}^{tu}\rangle &= |\cdots tu\cdots\rangle\end{aligned}$$

and applying Case 3 in Tables 2.3 and 2.4 in Szabo and Ostlund:

$$\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{ab}^{tu}\rangle = \langle rs||tu\rangle$$

Here we only considered a small subset of the total 36 combinations, but the same procedure used for this subset can be applied to the rest situations. In fact, one may not need to go through all combinations and still be able to "extrapolate" the general expression based on the patterns of a few subsets. The general expression for a matrix elements between two

arbitrary doubles is given below:

$$\begin{aligned}\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{cd}^{tu}\rangle = \delta_{ac}\delta_{bd}\delta_{rt}\delta_{su}(E_0-\varepsilon_a-\varepsilon_b+\varepsilon_r+\varepsilon_s)+\delta_{ac}\delta_{bd}\langle rs||tu\rangle+\delta_{rt}\delta_{su}\langle ab||cd\rangle \\ -\delta_{ac}\Big(\delta_{su}\langle rd||tb\rangle+\delta_{rt}\langle sd||ub\rangle-\delta_{ru}\langle sd||tb\rangle-\delta_{st}\langle rd||ub\rangle\Big) \\ -\delta_{bd}\Big(\delta_{su}\langle rc||ta\rangle+\delta_{rt}\langle sc||ua\rangle-\delta_{ru}\langle sc||ta\rangle-\delta_{st}\langle rc||ua\rangle\Big) \\ -\delta_{ad}\Big(-\delta_{su}\langle rc||tb\rangle-\delta_{rt}\langle sc||ub\rangle+\delta_{ru}\langle sc||tb\rangle+\delta_{st}\langle rc||ub\rangle\Big) \\ -\delta_{bc}\Big(-\delta_{su}\langle rd||ta\rangle-\delta_{rt}\langle sd||ua\rangle+\delta_{ru}\langle sd||ta\rangle+\delta_{st}\langle rd||ua\rangle\Big)\end{aligned}$$

where the symbols $\Delta_{ab,cd}$ and $\Delta_{rs,tu}$ are introduced for the sake of brevity, and they are defined as

$$\begin{aligned}\Delta_{ab,cd} &= \delta_{ac}\delta_{bd}-\delta_{ad}\delta_{bc} \\ \Delta_{rs,tu} &= \delta_{rt}\delta_{su}-\delta_{ru}\delta_{st}\end{aligned}$$

2.7 Conclusion

So far we have applied the Slater-Condon rules and derived the general CI matrix elements involving determinants up to double excitations. The resutls are summarized in Tab. 2. As a final remark for concluding this section, the use of Slater-Condon rules can be very straightforward and efficient in evaluating matrix elements with *definite* determinants. However, for *indefinite* matrix elements the evaluation of all possible situations can be a very tedious process, and it will become even worse for matrix elements involving triple or higher excitations.

Table 2. CI matrix elements (up to double excitations) in the determinantal basis

$$
\begin{aligned}
\langle\Psi_0|\hat{H}|\Psi_0\rangle = \quad & E_0 \\
\langle\Psi_0|\hat{H}|\Psi_a^r\rangle = \quad & 0 \\
\langle\Psi_a^r|\hat{H}|\Psi_b^s\rangle = \quad & \delta_{ab}\delta_{rs}(E_0 - \varepsilon_a + \varepsilon_r) - \langle rb||sa\rangle \\
\langle\Psi_0|\hat{H}|\Psi_{ab}^{rs}\rangle = \quad & \langle ab||rs\rangle \\
\langle\Psi_a^r|\hat{H}|\Psi_{bc}^{st}\rangle = \quad & \delta_{ab}\langle rc||st\rangle - \delta_{ac}\langle rb||st\rangle + \delta_{rs}\langle bc||ta\rangle - \delta_{rt}\langle bc||sa\rangle \\
\langle\Psi_{ab}^{rs}|\hat{H}|\Psi_{cd}^{tu}\rangle = \quad & \delta_{ac}\delta_{bd}\delta_{rt}\delta_{su}(E_0 - \varepsilon_a - \varepsilon_b + \varepsilon_r + \varepsilon_s) \\
& +\delta_{ac}\delta_{bd}\langle rs||tu\rangle + \delta_{rt}\delta_{su}\langle ab||cd\rangle \\
& -\delta_{ac}\Big(\delta_{su}\langle rd||tb\rangle + \delta_{rt}\langle sd||ub\rangle - \delta_{ru}\langle sd||tb\rangle - \delta_{st}\langle rd||ub\rangle\Big) \\
& -\delta_{bd}\Big(\delta_{su}\langle rc||ta\rangle + \delta_{rt}\langle sc||ua\rangle - \delta_{ru}\langle sc||ta\rangle - \delta_{st}\langle rc||ua\rangle\Big) \\
& -\delta_{ad}\Big(-\delta_{su}\langle rc||tb\rangle - \delta_{rt}\langle sc||ub\rangle + \delta_{ru}\langle sc||tb\rangle + \delta_{st}\langle rc||ub\rangle\Big) \\
& -\delta_{bc}\Big(-\delta_{su}\langle rd||ta\rangle - \delta_{rt}\langle sd||ua\rangle + \delta_{ru}\langle sd||ta\rangle + \delta_{st}\langle rd||ua\rangle\Big)
\end{aligned}
$$