Matrix Elements in Second Quantization

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July 2023

In the last section, we have seen that matrix elements in second quantization are given by vacuum expectation values of strings of ladder operators. It is probably not surprising that their is a neat trick to evaluate such matrix elements, since the whole point of second quantization is to make calculations easier.

1 Normal Ordering and Wick's Theorem

Let us at first inspect the following matrix element:

$$\langle \text{vac} | a^\dagger_{r_1} \cdots a^\dagger_{r_k} a_{s_1} \cdots a_{s_l} | \text{vac} \rangle$$

Although the string is quite long, it is not hard to evaluate the matrix element, since the right vacuum state is destroyed by the annihilation operators and the left vacuum state is destroyed by the creation operators.

Strings in such order, i.e. with all creation operators to the left of all annihilation operators, are called *normal ordered*. The vacuum expectation value of a normal ordered string is always zero. We denote a string to be normal ordered using $:\cdot:$, where the dot stands for the string. This notation introduces a sign $(-1)^p$, where p is the number of fermionic operators that have to be passed to reach the normal order.

We can now define a *contraction* of two operators as the pair itself minus the normal ordered pair, i.e.

$$\overbrace{a^{(\dagger)}_p a^{(\dagger)}_q} = a^{(\dagger)}_p a^{(\dagger)}_q - :a^{(\dagger)}_p a^{(\dagger)}_q:$$

It is obvious that a contraction between two operators already in normal order is zero. So the only non-zero contraction is

$$\overbrace{a_p a^\dagger_q} = a_p a^\dagger_q - :a_p a^\dagger_q: = a_p a^\dagger_q + a^\dagger_q a_p = \delta_{pq}$$

A sign change occurs because the creation operator has to be moved pass one fermion operator to reach the normal order.

A contraction between two operators separated by fermionic operators is defined as

$$\overbrace{a^{(\dagger)}_p a^{(\dagger)}_{r_1} \cdots a^{(\dagger)}_{r_n} a^{(\dagger)}_q} = (-1)^n \, \overbrace{a^{(\dagger)}_p a^{(\dagger)}_q} \, a^{(\dagger)}_{r_1} \cdots a^{(\dagger)}_{r_n}$$

So, the following example can be evaluated as

$$\overbrace{a_p a_r a_q^\dagger} a_s^\dagger = (-1)\, \overbrace{a_p a_q^\dagger}\, a_r a_s^\dagger = -\delta_{pq} a_r a_s^\dagger$$

So it seems that a contraction can simplify the string, or, to use some technical jargons, reduce the rank of the string. It would be nice if we could somehow represent the string as a sum of contractions. This is precisely the statement of Wick's theorem:

$$\begin{aligned} a_p^{(\dagger)} a_q^{(\dagger)} a_r^{(\dagger)} \cdots a_s^{(\dagger)} a_t^{(\dagger)} a_u^{(\dagger)} = \; & :a_p^{(\dagger)} a_q^{(\dagger)} a_r^{(\dagger)} \cdots a_s^{(\dagger)} a_t^{(\dagger)} a_u^{(\dagger)}: \\ & + \sum_{\text{singles}} :\overbrace{a_p^{(\dagger)} a_q^{(\dagger)}}\, a_r^{(\dagger)} \cdots a_s^{(\dagger)} a_t^{(\dagger)} a_u^{(\dagger)}: \\ & + \sum_{\text{doubles}} :\overbrace{a_p^{(\dagger)} a_q^{(\dagger)} a_r^{(\dagger)} \cdots a_s^{(\dagger)}}\, a_t^{(\dagger)} a_u^{(\dagger)}: \\ & + \cdots \end{aligned}$$

where "singles", "doubles", etc. refer to the number of pairwise contractions.

This means that we can write an arbitrary string as a sum of it normal ordered form and all possible contractions in normal order. At first glance, this theorem seems to be of little use, since we have made an already complicated expression even more complicated. But since normal ordered string will always give zero when sandwiched between two vacuum states, any term in the sum that has a normal ordered string do not contribute to the matrix element. This leaves us with only the terms where all the operators are pairwise contracted, the so-called *fully contracted* strings.

So instead of painfully manipulating the string using anticommutation relations, we can simply write down all the fully contracted strings. Since the contraction will just give us a bunch of Kronecker deltas, which are just numbers, we do not have to worry about how the states look like at all. This is the power of Wick's theorem.

Let us do an example. Consider the two one-electron states $|t\rangle = a_t^\dagger|\text{vac}\rangle$ and $|u\rangle = a_u^\dagger|\text{vac}\rangle$. The matrix element of a one-electron operator $\hat{O}_1 = \sum_{pq} o_{pq} a_p^\dagger a_q$ can be easily evalulated by retaining only the fully contracted strings:

$$\begin{aligned} \langle t|\hat{O}_1|u\rangle &= \langle t| \sum_{pq} o_{pq} a_p^\dagger a_q |u\rangle \\ &= \sum_{pq} o_{pq} \langle \text{vac}| a_t a_p^\dagger a_q a_u^\dagger |\text{vac}\rangle \\ &= \sum_{pq} o_{pq}\, \overbrace{a_t a_p^\dagger}\, \overbrace{a_q a_u^\dagger} \\ &= \sum_{pq} o_{pq} \delta_{tp} \delta_{qu} \\ &= o_{tu} \end{aligned}$$

identical to the result we would obtain using Slater-Condon rules. Note that we did not really have to evaluate all possible full contractions, since only contractions with annihilation operators on the left and creation operators on the right are nonzero.

¿ There is a interesting rule about the sign of fully contracted strings. If ¿ the number of crossings made by the lines representing contractions is even, ¿ the overall sign is positive; if the number of crossings is odd, the overall ¿ sign is negative.

These rules might work very well for particle physisists, who only have to worry about a handful of particles. But for chemists, who have to deal with molecular systems with hundreds of electrons. If we have to reduce all states to the true vacuum state when evaluating matrix elements, we would have to deal with a very very long string. This is where the concept of Fermi vacuum comes in. Instead of using the true vacuum as the reference we can use an arbitrary Slater determinant. To achieve this, we only have to alter our operators a little.

Because our reference state can now contain occupied sites, not every annihilation operator will destroy it, while some creation operators can destroy it. Therefore, we define two classes of ladder operators, namely particle operators and hole operators. The particle creators $a_a^\dagger$ and annihilators a_a creates a particle and removes a particle, respectively. The hole creators a_i and annihilators $a_i^\dagger$ creates a hole (by removing a particle from a occupied site) and annihilates a hole (by adding an electron to an unoccupied site), respectively. We will adopt the convention from now on, that the indices $i, j, k, \cdots$ refer to occupied sites, the indices $a, b, c, \cdots$ refer to unoccupied sites, and the indices $p, q, r, \cdots$ refer to general sites.

Since holes can not be called a particle with the best will in the world, we shall use the more general term *quasiparticles* and call the new operators quasiparticle operators or q-operators for short. A string is called to be normal ordered relative to the Fermi vacuum if all the q-creators are standing to the left of all q-annihilators. We will just call this normal ordering from now on.

With a bit of thought, we can see that the only nonzero contractions between q-operators are

$$\overbracket{a_i^\dagger a_j} = a_i^\dagger a_j - :a_i^\dagger a_j: = a_i^\dagger a_j + a_j a_i^\dagger = \delta_{ij}$$
$$\overbracket{a_a a_b^\dagger} = a_a a_b^\dagger - :a_a a_b^\dagger: = a_a a_b^\dagger + a_b^\dagger a_a = \delta_{ab}$$

Contractions with q-creators on the left and q-annihilators on the right, as well as with mixed hole particle operators, are zero.

So, by using q-operators instead of ordinary operators, we can work with Fermi vacuum as we have worked with true vacuum. In many quantum chemical calculations, the Hartree-Fock wavefunction as the reference state, which is a Slater determinant. Therefore, Fermi vacuum and q-operators can be very useful in deriving the expressions of matrix elements.

2 CIS Revisited

Now we are ready to revisit the CIS method and derive the CIS equation using the language of second quantization. We shall at first bring the Hamiltonian into normal order. Although this is not necessary for the derivation, but will make our results more intepretable.

Let us examine the one-electron part at first. Using Wick's theorem, we obtain

$$\begin{aligned}\sum_{pq} h_{pq} a_p^\dagger a_q &= \sum_{pq} h_{pq} :a_p^\dagger a_q: + \sum_{pq} h_{pq} :\overbracket{a_p^\dagger} a_q: \\ &= \sum_{pq} h_{pq} :a_p^\dagger a_q: + \sum_{ij} h_{ij}\delta_{ij} \\ &= \sum_{pq} h_{pq} :a_p^\dagger a_q: + \sum_{i} h_{ii}\end{aligned}$$

Since the contraction will only be nonzero if p and q are both occupied, we can identify the indices with i and j.

The two-electron part is a bit more complicated, but it follows the same principle:

$$\begin{aligned}&\frac{1}{2}\sum_{pqrs} g_{pqrs} a_p^\dagger a_r^\dagger a_s a_q \\ =\ &\frac{1}{2}\Big[\sum_{pqrs} g_{pqrs} :a_p^\dagger a_r^\dagger a_s a_q: \\ &\quad + \sum_{pqrs} g_{pqrs} :\overbracket{a_p^\dagger a_r^\dagger} a_s a_q: + \sum_{pqrs} g_{pqrs} :\overbracket{a_p^\dagger a_r^\dagger a_s} a_q: + \sum_{pqrs} g_{pqrs} :a_p^\dagger \overbracket{a_r^\dagger a_s} a_q: \\ &\quad + \sum_{pqrs} g_{pqrs} :a_p^\dagger \overbracket{a_r^\dagger a_s a_q}: + \sum_{pqrs} g_{pqrs} :\overbracket{a_p^\dagger a_r^\dagger} \overbracket{a_s a_q}: + \sum_{pqrs} g_{pqrs} :\overbracket{a_p^\dagger \overbracket{a_r^\dagger a_s} a_q}: \Big] \\ =\ &\frac{1}{2}\Big[\sum_{pqrs} g_{pqrs} :a_p^\dagger a_r^\dagger a_s a_q: \\ &\quad - \sum_{iqr} g_{iqri} :a_r^\dagger a_q: + \sum_{irs} g_{iirs} :a_r^\dagger a_s: + \sum_{pqi} g_{pqii} :a_p^\dagger a_q: \\ &\quad - \sum_{pis} g_{piis} :a_p^\dagger a_s: - \sum_{ij} g_{ijji} + \sum_{ij} g_{iijj} \Big] \\ =\ &\frac{1}{2}\sum_{pqrs} g_{pqrs} :a_p^\dagger a_r^\dagger a_s a_q: + \sum_{ipq} (g_{iipq} - g_{ipqi}) :a_p^\dagger a_q: + \frac{1}{2}\sum_{ij} (g_{iijj} - g_{ijji})\end{aligned}$$

where we renamed some summation indices and used the symmetry $g_{pqrs} = g_{rspq}$ in the last step.

Now we can identify

$$\sum_i h_{ii} + \frac{1}{2}\sum_{ij}(g_{iijj} - g_{ijji}) = E_{\mathrm{HF}} \quad \text{HF energy}$$
$$h_{pq} + \sum_i (g_{iipq} - g_{ipqi}) = f_{pq} \quad \text{Fock matrix element}$$

and write the Hamiltonian as

$$\begin{aligned}\hat{H} &= \sum_{pq} f_{pq} :a_p^\dagger a_q: + \frac{1}{2}\sum_{pqrs} g_{pqrs} :a_p^\dagger a_r^\dagger a_s a_q: + E_{\mathrm{HF}} \\ &= \hat{F}_N + \hat{V}_N + E_{\mathrm{HF}}\end{aligned}$$

We can now take a look at the matrix elements of the CIS Hamiltonian.

2.1 $\langle\Phi_0|\hat{H}|\Phi_0\rangle$

Since Φ_0 is the Fermi vacuum, and the first two terms of the Hamiltonian are normal ordered, they do not contribute to the matrix element. Therefore,

$$\langle\Phi_0|\hat{H}|\Phi_0\rangle = \langle\Phi_0|E_{\mathrm{HF}}|\Phi_0\rangle = E_{\mathrm{HF}}$$

2.2 $\langle\Phi_0|\hat{H}|\Phi_i^a\rangle$

We at first take a look at the one-electron part:

$$\begin{aligned}\langle\Phi_0|\hat{F}_N|\Phi_i^a\rangle &= \sum_{pq} f_{pq}\langle\Phi_0| :a_p^\dagger a_q: a_a^\dagger a_i|\Phi_0\rangle \\ &= \sum_{pq} f_{pq}\langle\Phi_0| :\overbrace{a_p^\dagger \overbrace{a_q a_a^\dagger}} a_i: |\Phi_0\rangle \\ &= \sum_{pq} f_{pq}\langle\Phi_0|\delta_{pi}\delta_{qa}|\Phi_0\rangle \\ &= f_{ia}\end{aligned}$$

Because only fully contracted string contribute to the matrix element, and contractions within a normal ordered string are zero, we only have to consider one contraction. Because it has zero crossings, its sign is positive.

For the two-electron part, because only two ladder operators are not within the normal ordered part, we can at most have nonzero double contractions. But because we have 6 ladder operators in total, these contractions cannot be full contractions and therefore do not contribute to the matrix element.

The zero-electron part is easy:

$$\langle\Phi_0|E_{\mathrm{HF}}|\Phi_i^a\rangle = E_{HF}\langle\Phi_0|a_a^\dagger a_i|\Phi_0\rangle = 0$$

Wrapping everything up, we get

$$\langle\Phi_0|\hat{H}|\Phi_i^a\rangle = f_{ia}$$

If the sites are HF orbitals, the converged Fock matrix is diagonal and thus f_{ia}, which is certainly off-diagonal, is zero. We have hereby shown Brillouin's theorem.

2.3 $\langle\Phi_i^a|\hat{H}|\Phi_j^b\rangle$

Again, we start with the one-electron part:

$$\begin{aligned}
\langle\Phi_i^a|\hat{F}_N|\Phi_j^b\rangle &= \sum_{pq} f_{pq}\langle\Phi_0|a_i^\dagger a_a :a_p^\dagger a_q: a_b^\dagger a_j|\Phi_0\rangle \\
&= \sum_{pq} f_{pq}\Big[\langle\Phi_0| :a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j: |\Phi_0\rangle + \langle\Phi_0| :a_i^\dagger a_a a_p^\dagger a_q a_b^\dagger a_j: |\Phi_0\rangle\Big] \\
&= -\sum_{lk} f_{lk}\langle\Phi_0|\delta_{ik}\delta_{ab}\delta_{lj}|\Phi_0\rangle + \sum_{cd} f_{cd}\langle\Phi_0|\delta_{ij}\delta_{ac}\delta_{db}|\Phi_0\rangle \\
&= -f_{ji}\delta_{ab} + f_{ab}\delta_{ij} \\
&= f_{ab}\delta_{ij} - f_{ij}^*\delta_{ab}
\end{aligned}$$

The minus sign appears because the first contraction has three crossings.

Then, we move to the two-electron part:

$$\begin{aligned}
\langle\Phi_i^a|\hat{V}_N|\Phi_j^b\rangle &= \frac{1}{2}\sum_{pqrs} g_{pqrs}\langle\Phi_0|a_i^\dagger a_a :a_p^\dagger a_r^\dagger a_s a_q: a_b^\dagger a_j|\Phi_0\rangle \\
&= \frac{1}{2}\Big[\sum_{pqrs} g_{pqrs}\langle\Phi_0| :a_i^\dagger a_a a_p^\dagger a_r^\dagger a_s a_q a_b^\dagger a_j: |\Phi_0\rangle \\
&\quad + \sum_{pqrs} g_{pqrs}\langle\Phi_0| :a_i^\dagger a_a a_p^\dagger a_r^\dagger a_s a_q a_b^\dagger a_j: |\Phi_0\rangle \\
&\quad + \sum_{pqrs} g_{pqrs}\langle\Phi_0| :a_i^\dagger a_a a_p^\dagger a_r^\dagger a_s a_q a_b^\dagger a_j: |\Phi_0\rangle \\
&\quad + \sum_{pqrs} g_{pqrs}\langle\Phi_0| :a_i^\dagger a_a a_p^\dagger a_r^\dagger a_s a_q a_b^\dagger a_j: |\Phi_0\rangle\Big] \\
&= \frac{1}{2}\Big[-\sum_{cdlk} g_{cdlk}\langle\Phi_0|\delta_{ik}\delta_{ac}\delta_{lj}\delta_{db}|\Phi_0\rangle + \sum_{ldck} g_{ldck}\langle\Phi_0|\delta_{ik}\delta_{ac}\delta_{lj}\delta_{db}|\Phi_0\rangle \\
&\quad + \sum_{ckld} g_{ckld}\langle\Phi_0|\delta_{ik}\delta_{ac}\delta_{lj}\delta_{db}|\Phi_0\rangle - \sum_{lkcd} g_{lkcd}\langle\Phi_0|\delta_{ik}\delta_{ac}\delta_{lj}\delta_{db}|\Phi_0\rangle\Big] \\
&= \frac{1}{2}(-g_{abji} + g_{jbai} + g_{aijb} - g_{jiab}) \\
&= g_{jbai} - g_{jiab}
\end{aligned}$$

Again, the zero-electron part is easy:

$$\langle \Phi_i^a | E_{\mathrm{HF}} | \Phi_j^b \rangle = E_{\mathrm{HF}} \langle \Phi_0 | \, \overbrace{a_i^\dagger a_a a_b^\dagger} a_j \, | \Phi_0 \rangle = E_{\mathrm{HF}} \delta_{ij} \delta_{ab}$$

Putting everything together, we get

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle = f_{ab} \delta_{ij} - f_{ij}^* \delta_{ab} + g_{jbai} - g_{jiab} + E_{\mathrm{HF}} \delta_{ij} \delta_{ab}$$

If the sites are HF orbitals, we again have a diagonal Fock matrix, so the matrix elements $f_{ab} = f_{aa}\delta_{ab}$ and $f_{ij} = f_{ii}\delta_{ij}$. The diagonal elements f_{aa} and f_{ii} can be identified as orbital energies ϵ_a and ϵ_i, respectively. Therefore, we obtain

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle = (E_{\mathrm{HF}} + \epsilon_a - \epsilon_i) \delta_{ij} \delta_{ab} + g_{jbai} - g_{jiab}$$

which we have used to implement our CIS routine.