Lecture 3.6: a_p and $a_p^\dagger$ in the Particle-Hole Formalism

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Previously, we saw that to work in the Fermi vacuum, we could first translate particle operators a_p and $a_p^\dagger$ into quasiparticle operators b_p and $b_p^\dagger$. This was not efficient because for each p there are two cases to consider: occupied and unoccupied. For a string of 4 operators, $a_p^\dagger a_q^\dagger a_s a_r$, this would mean we have 16 terms in the particle-hole formalism to deal with. Instead, we want to work directly with a_p and $a_p^\dagger$ in the particle-hole formalism. Our next task is to see how to do that.

1 Working with a_p and $a_p^\dagger$ in the particle-hole formalism

1.1 Anticommuntation relations

The anticommuntation relations for a_p and $a_p^\dagger$ stays the same. Strictly speaking, we see that the definitions depend on what the index p is, for example:

$$a_i, a_a = b_i^\dagger, b_a = \delta_{ia}$$

However, this quantity ends up being 0 because δ_{ia} is always 0. We can make this sort of argument for all mixed cases of occupied and unoccupied indices to see that the anticommuntation relations remains:

1. $\{a_p, a_q\} = 0$
2. $\{a_p^\dagger, a_q^\dagger\} = 0$
3. $\{a_p, a_q^\dagger\} = \delta_{pq}$

1.2 Φ-Normal products using a_p and $a_p^\dagger$

How do we evaluate $N[a_p^\dagger a_q a_r^\dagger]$? We need to translate back to quasiparticle operators. In order to do that, we have to specify occupation for the indices.

In the case where $p = i$, $q = j$, and $r = a$,

$$\begin{aligned} N[a_i^\dagger a_j a_a^\dagger] &= N[b_i b_j^\dagger b_a^\dagger] \\ &= b_j^\dagger b_a^\dagger b_i \\ &= a_j a_a^\dagger a_i^\dagger \\ &\neq n[a_i^\dagger a_j a_a^\dagger] \end{aligned}$$

Thus, we see that $N[x_1 \cdots x_m] \neq n[x_1 \cdots x_m]$, and the relationship between the two depends on the indices.

A formal definition for the normal product is:

$$N[x_1 \cdots x_m] = (-1)^R b_{R_1}^\dagger \cdots b_{R_\alpha}^\dagger b_{R_{\alpha+1}} \cdots b_{R_m}$$

Thus, a Φ-normal product using a_p and $a_p^\dagger$ still means that all the quasiparticle operators $b_p^\dagger$ are to the left and b_p are to the right. In order to explicitly write a form for $N[x_1 \cdots x_m]$, we would need to know the occupation of the indices.

1.3 Contractions in the Fermi vacuum using a_p and $a_p^\dagger$

To figure out what contractions between a_p and $a_p^\dagger$ look like with respect to the Fermi vacuum, we first introduce the step functions χ and π:

$$\chi(p) = \begin{cases} 1 & p \in \textit{occupied} \\ 0 & p \in \textit{unoccupied} \end{cases}$$

$$\pi(p) = \begin{cases} 0 & p \in \textit{occupied} \\ 1 & p \in \textit{unoccupied} \end{cases}$$

For example,

$$\chi(i) = 1 \qquad \chi(a) = 0 \qquad \pi(i) = 0 \qquad \pi(a) = 1$$

The step functions have the following properties:

$$\chi(p) + \pi(p) = 1$$

$$\chi(p)\pi(p) = 0$$
$$\chi^2(p) = \chi(p)$$
$$\pi^2(p) = \pi(p)$$

We can use the step functions to inform how to map between particle operators and quasiparticle operators. For example, $\chi(p)a_p = b_p^\dagger$.

Let's see how we can figure out how to compute a contraction in the Fermi vacuum for a_p and a_q:

$$\begin{aligned} \overbracket{a_p a_q} &= (1)(1)\overbracket{a_p a_q} \\ &= [\chi(p) + \pi(p)][\chi(q) + \pi(q)]\overbracket{a_p a_q} \\ &= \chi(p)\chi(q)\overbracket{a_p a_q} + \chi(p)\pi(q)\overbracket{a_p a_q} + \pi(p)\chi(q)\overbracket{a_p a_q} + \pi(p)\pi(q)\overbracket{a_p a_q} \end{aligned}$$

Now, the step functions will inform what b operator to translate to:

$$\begin{aligned} \overbracket{a_p a_q} &= \chi(p)\chi(q)\overbracket{a_p a_q} + \chi(p)\pi(q)\overbracket{a_p a_q} + \pi(p)\chi(q)\overbracket{a_p a_q} + \pi(p)\pi(q)\overbracket{a_p a_q} \\ &= \chi(p)\chi(q)\overbracket{b_p^\dagger b_q^\dagger} + \chi(p)\pi(q)\overbracket{b_p^\dagger b_q} + \pi(p)\chi(q)\overbracket{b_p b_q^\dagger} + \pi(p)\pi(q)\overbracket{b_p b_q} \end{aligned}$$

we can get rid of all contractions that go to zero

$$\begin{aligned} &= \cancelto{0}{\chi(p)\chi(q)\overbracket{b_p^\dagger b_q^\dagger}} + \cancelto{0}{\chi(p)\pi(q)\overbracket{b_p^\dagger b_q}} + \pi(p)\chi(q)\overbracket{b_p b_q^\dagger} + \cancelto{0}{\pi(p)\pi(q)\overbracket{b_p b_q}} \\ &= \pi(p)\chi(q)\delta_{pq} \\ &= \pi(p)\chi(p) \\ &= 0 \end{aligned}$$

We can take the same steps to find $\overbrace{a_p^\dagger a_q}$:

$$\begin{aligned}
\overbrace{a_p^\dagger a_q} &= [\chi(p) + \pi(p)][\chi(q) + \pi(q)]\overbrace{a_p^\dagger a_q} \\
&= \chi(p)\chi(q)\overbrace{a_p^\dagger a_q} + \chi(p)\pi(q)\overbrace{a_p^\dagger a_q} + \pi(p)\chi(q)\overbrace{a_p^\dagger a_q} + \pi(p)\pi(q)\overbrace{a_p^\dagger a_q} \\
&= \chi(p)\chi(q)\overbrace{b_p b_q^\dagger} + \chi(p)\pi(q)\overbrace{b_p b_q} + \pi(p)\chi(q)\overbrace{b_p^\dagger b_q^\dagger} + \pi(p)\pi(q)\overbrace{b_p^\dagger b_q} \\
&= \chi(p)\chi(q)\overbrace{b_p b_q^\dagger} + \cancel{\chi(p)\pi(q)\overbrace{b_p b_q}}^{0} + \cancel{\pi(p)\chi(q)\overbrace{b_p^\dagger b_q^\dagger}}^{0} + \cancel{\pi(p)\pi(q)\overbrace{b_p^\dagger b_q}}^{0} \\
&= \chi(p)\chi(q)\delta_{pq} \\
&= \chi(p)\chi(p)\delta_{pq} \\
&= \chi^2(p)\delta_{pq} \\
&= \chi(p)\delta_{pq} \\
&= \gamma_{pq}
\end{aligned}$$

We can do the same type of derivation for $\overbrace{a_p a_q^\dagger}$ and $\overbrace{a_p^\dagger a_q^\dagger}$. You will practice this in your homework. The end result is:

$$\overbrace{a_p a_q} = 0$$

$$\overbrace{a_p a_q^\dagger} = \pi(p)\delta_{pq} = \eta_{pq}$$

$$\overbrace{a_p^\dagger a_q} = \chi(p)\delta_{pq} = \gamma_{pq}$$

$$\overbrace{a_p^\dagger a_q^\dagger} = 0$$

where we have defined $\eta_{pq} = \pi(p)\delta_{pq}$ and $\gamma_{pq} = \chi(p)\delta_{pq}$.

1.4 Φ-Normal products using a_p and $a_p^\dagger$

From what we know so far, we see that a Φ-normal product with contractions inside for particle operators

$$N[x_1 \cdots \overbrace{x_{i_1} \cdots \overbrace{x_{i_\lambda} \cdots x_{j_1}} \cdots x_{j_\lambda}} \cdots x_m]$$

can be rewritten as:

$$N[x_1 \cdots \overbrace{x_{i_1} \cdots \overbrace{x_{i_\lambda} \cdots x_{j_1}} \cdots x_{j_\lambda}} \cdots x_m] = (-1)^R \overbrace{x_{i_1} x_{j_1}} \cdots \overbrace{x_{i_\lambda} x_{j_\lambda}} N[x_{k_1} \cdots x_{k_\mu}]$$

where

$$R = \begin{pmatrix} 1 & 2 & \cdots & 2\lambda - 1 & 2\lambda & 2\lambda + 1 & \cdots & m \\ i_1 & j_1 & \cdots & i_\lambda & j_\lambda & k_1 & \cdots & k_\mu \end{pmatrix}$$

and the indices $2\lambda + \mu = m$.

For example:

$$\begin{aligned}
N[\overbrace{a_p^\dagger a_q a_r^\dagger a_s} a_t a_u^\dagger] &= \overbrace{a_p^\dagger a_s} \overbrace{a_q a_r^\dagger} \overbrace{a_t a_u^\dagger} \\
&= [\chi(p)\delta_{ps}][\pi(p)\delta_{qr}][\pi(t)\delta_{tu}] \\
&= \gamma_{ps}\eta_{qr}\eta_{tu}
\end{aligned}$$

1.5 Wick's Theorem

Now that we have addressed what Φ-normal ordering and Φ-normal ordering with contractions mean for operators a_p and $a_p^\dagger$, we are ready to state Wick's theorem for a_p and $a_p^\dagger$ in the particle-hole formalism:

$$x_1 \cdots x_m = N[x_1 \cdots x_m] + \sum_{a.c.} N\overline{[x_1 \cdots x_m]}$$

The generalized Wick's Theorem states:

$$x_1 \cdots N[x_\nu \cdots x_\mu] \cdots x_m = N[x_1 \cdots x_m] + \sum_{a.c.}{}' N\overline{[x_1 \cdots x_m]}$$

Where $\sum_{a.c.}{}'$ stands for all possible contractions except the ones between the operators within the Φ-normal order.

1.6 Rules for expectation values

We can now see what the rules imply for a_p and $a_p^\dagger$ in the Fermi vacuum.

- Rule 1: $N[x_1 \cdots x_m]\,|\Phi\rangle = 0$ unless $x_1 \cdots x_m$ only contains a_p where $p \in occ$ and $a_q^\dagger$ where $q \in unocc$.
- Rule 2: $\langle\Phi|N[x_1 \cdots x_m]|\Phi\rangle = 0$ for $m \geq 1$
- Rule 3. $N[x_1 \cdots \overbrace{x_{\nu_1} \cdots \overbrace{x_{\nu_\lambda} \cdots x_{\mu_1}} \cdots x_{\mu_\lambda}} \cdots x_m]\,|\Phi\rangle = 0$ if there is at least 1 uncontracted operator $a_p^\dagger$ where $p \in occ$ or a_q where $q \in unocc$
- Rule 4. $\langle\Phi|\,N[x_1 \cdots \overbrace{x_{\nu_1} \cdots \overbrace{x_{\nu_\lambda} \cdots x_{\mu_1}} \cdots x_{\mu_\lambda}} \cdots x_m]\,|\Phi\rangle = 0$ unless all operators are contracted. A vacuum expectation value of any normal product with contractions will be zero if there are a odd number of operators.
- Rule 5 $\langle\Phi|x_1 \cdots x_{2m+1}|\Phi\rangle = 0$
- Rule 6 $\langle\Phi|x_1 \cdots x_{2m}|\Phi\rangle = \sum_{f.c.} \langle\Phi|N\overline{\overline{[x_1 \cdots x_{2m}]}}|\Phi\rangle = \sum_{f.c.} (-1)^R \overbrace{x_{\nu_1} x_{\mu_1}} \cdots \overbrace{x_{\nu_m} x_{\mu_m}}$

$$R = \begin{pmatrix} 1 & 2 & \cdots & 2m-1 & 2m \\ \nu_1 & \mu_1 & \cdots & \nu_m & \mu_m \end{pmatrix}$$

- Rule 7 $x_1 \cdots x_m\,|\Phi\rangle = \sum_{b_p f.c.} N\overline{[x_1 \cdots x_m]}\,|\Phi\rangle$ where $\sum_{b_p f.c.}$ denotes that any $a_p^\dagger$ where $p \in occ$ or a_q where $q \in unocc$ is fully contracted.

1.7 Example: Deriving Slater's first rule

We can use what we have learned so far to quickly derive Slater's first rule.

$$\langle\Phi|H|\Phi\rangle = \langle\Phi|\sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle\, a_p^\dagger a_q^\dagger a_s a_r|\Phi\rangle$$

One-electron term:

$$\begin{aligned}\sum_{pq} h_{pq} \langle\Phi|a_p^\dagger a_q|\Phi\rangle &= \sum_{pq} h_{pq} \langle\Phi|N[\overbrace{a_p^\dagger a_q}]|\Phi\rangle) \\ &= \sum_{pq} h_{pq}\chi(p)\delta_{pq} \langle\Phi|\Phi\rangle \\ &= \sum_{pq} h_{pq}\gamma_{pq} \\ &= \sum_{ij} h_{ij}\delta_{ij} \\ &= \sum_{i} h_{ii}\end{aligned}$$

Two-electron term:

$$\begin{aligned}\frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle \langle\Phi|a_p^\dagger a_q^\dagger a_s a_r|\Phi\rangle &= \frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle \sum_{f.c.} \langle\Phi|N[\overbrace{\overbrace{a_p^\dagger a_q^\dagger a_s a_r}}]|\Phi\rangle \\ &= \frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle \left(\langle\Phi|N[\overbrace{a_p^\dagger \overbrace{a_q^\dagger a_s} a_r}]|\Phi\rangle + \langle\Phi|N[\overbrace{a_p^\dagger \overbrace{a_q^\dagger a_s} a_r}]|\Phi\rangle\right) \\ &= \frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle \left(\gamma_{pr}\gamma_{qs} - \gamma_{ps}\gamma_{qr}\right) \\ &\quad \text{make assignments } p \to i \quad q \to j \quad r \to k \quad s \to l \\ &= \frac{1}{2}\sum_{ijkl} \langle ij|kl\rangle \left(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}\right) \\ &= \frac{1}{2}\sum_{ij} \langle ij|ij\rangle - \langle ij|ji\rangle \\ &= \frac{1}{2}\sum_{ij} \langle ij||ij\rangle\end{aligned}$$

What if we wanted to solve for matrix elements of terms like $\langle\Phi_{kl}^{cd}|H|\Phi_{ij}^{ab}\rangle$? This means we are working with 12 operators:

$$\langle\Phi|a_l^\dagger a_d a_k^\dagger a_c a_p^\dagger a_q^\dagger a_s a_r a_a^\dagger a_i a_b^\dagger a_j|\Phi\rangle$$

Previously, in the particle formalism, we took advantage of the Generalized Wick's theorem to reduce the number of contractions we have to consider. We only considered contractions between operators that were not from the same normal-ordered group. We see that if we could put different groups in the above term in Φ-normal ordering, we can reduce the number of terms we have to consider.

2 Excitation operators from $|\Phi\rangle$ are already in Φ-normal order

We see that the operators associated with excitations from the reference determinant are already in Φ-normal order.

For example,

$$a_a^\dagger a_i a_b^\dagger a_j = b_a^\dagger b_i^\dagger b_b^\dagger b_j^\dagger = N[b_a^\dagger b_i^\dagger b_b^\dagger b_j^\dagger] = N[a_a^\dagger a_i a_b^\dagger a_j]$$

We see that using anticommuntation relations, we can also equivalently write:

$$N[b_a^\dagger b_i^\dagger b_b^\dagger b_j^\dagger] = N[b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger] = N[a_a^\dagger a_b^\dagger a_j a_i]$$

Both forms can be used to express excitations from the reference determinant.

3 The Φ-normal ordered Hamiltonian

We can use Wick's theorem to help put the Hamiltonian in Φ-normal order.

One-electron operator:

$$\begin{aligned}\hat{h} &= \sum_{pq} h_{pq} a_p^\dagger a_q \\ &= \sum_{pq} h_{pq} (N[a_p^\dagger a_q] + N[\overbrace{a_p^\dagger a_q}]) \\ &= \sum_{pq} h_{pq} N[a_p^\dagger a_q] + \sum_{pq} h_{pq} \gamma_{pq} \\ &= \sum_{pq} h_{pq} N[a_p^\dagger a_q] + \sum_{i} h_{ii}\end{aligned}$$

Two-electron operator:

$$\begin{aligned}\hat{g} &= \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle \, a_p^\dagger a_q^\dagger a_s a_r \\ &= \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle \, N[a_p^\dagger a_q^\dagger a_s a_r] \\ &\quad + \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle \left(N[\overbrace{a_p^\dagger a_q^\dagger} a_s a_r] + N[\overbrace{a_p^\dagger a_q^\dagger a_s} a_r] + N[a_p^\dagger \overbrace{a_q^\dagger a_s} a_r] + N[a_p^\dagger \overbrace{a_q^\dagger a_s a_r}] \right) \\ &\quad + \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle \left(N[\overbrace{a_p^\dagger \overbrace{a_q^\dagger} a_s} a_r] + N[\overbrace{a_p^\dagger \overbrace{a_q^\dagger a_s a_r}}] \right) \\ &= \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle \, N[a_p^\dagger a_q^\dagger a_s a_r] \\ &\quad + \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle \left(-\gamma_{ps} N[a_q^\dagger a_r] + \gamma_{pr} N[a_q^\dagger a_s] + \gamma_{qs} N[a_p^\dagger a_r] - \gamma_{qr} N[a_p^\dagger a_s] \right) \\ &\quad + \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle \left(\gamma_{pr}\gamma_{qs} - \gamma_{ps}\gamma_{qr} \right) \\ &= \frac{1}{2} \sum_{pqrs} \langle pq|rs\rangle \, N[a_p^\dagger a_q^\dagger a_s a_r] \\ &\quad - \frac{1}{2} \sum_{qr} \sum_{i} \langle iq|ri\rangle \, N[a_q^\dagger a_r] + \frac{1}{2} \sum_{qs} \sum_{i} \langle iq|is\rangle \, N[a_q^\dagger a_s] + \frac{1}{2} \sum_{pr} \sum_{i} \langle pi|ri\rangle \, N[a_p^\dagger a_r] - \frac{1}{2} \sum_{ps} \sum_{i} \langle pi|is\rangle \, N[a_p^\dagger a_s] \\ &\quad + \frac{1}{2} \sum_{ij} \langle ij||ij\rangle\end{aligned}$$

We can perform a change of variables and permute within the integrals:

$$\hat{g} = \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$
$$-\frac{1}{2}\sum_{pq}\sum_{i}\langle ip|qi\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{pq}\sum_{i}\langle ip|iq\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{pq}\sum_{i}\langle pi|qi\rangle\, N[a_p^\dagger a_q] - \frac{1}{2}\sum_{pq}\sum_{i}\langle pi|iq\rangle\, N[a_p^\dagger a_q]$$
$$+\frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

$$= \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$
$$\frac{1}{2}\sum_{pq}\sum_{i}\langle pi|qi\rangle\, N[a_p^\dagger a_q] - \frac{1}{2}\sum_{pq}\sum_{i}\langle pi|iq\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{pq}\sum_{i}\langle pi|qi\rangle\, N[a_p^\dagger a_q] - \frac{1}{2}\sum_{pq}\sum_{i}\langle pi|iq\rangle\, N[a_p^\dagger a_q]$$
$$+\frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

We can reorder the order of terms:

$$= \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$
$$+\frac{1}{2}\sum_{pq}\sum_{i}\langle pi|qi\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{pq}\sum_{i}\langle pi|qi\rangle\, N[a_p^\dagger a_q] - \frac{1}{2}\sum_{pq}\sum_{i}\langle pi|iq\rangle\, N[a_p^\dagger a_q] - \frac{1}{2}\sum_{pq}\sum_{i}\langle pi|iq\rangle\, N[a_p^\dagger a_q]$$
$$+\frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

$$= \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$
$$+\sum_{pq}\sum_{i}(\langle pi|qi\rangle - \langle pi|iq\rangle)N[a_p^\dagger a_q]$$
$$+\frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

$$= \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r] + \sum_{pq}\sum_{i}\langle pi||qi\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

All together, we get:

$$H = \sum_{pq} h_{pq} N[a_p^\dagger a_q] + \sum_i h_{ii} + \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r] + \sum_{pq}\sum_{i}\langle pi||qi\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle$$

We see that the second and fifth terms have no operators, and the first and fourth terms both have 2 operators. We can group these terms together:

$$H = \sum_i h_{ii} + \frac{1}{2}\sum_{ij}\langle ij||ij\rangle + \sum_{pq} h_{pq} N[a_p^\dagger a_q] + \sum_{pq}\sum_{i}\langle pi||qi\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$

The first two terms we see are simply $\langle\Phi|H|\Phi\rangle$:

$$H = \langle\Phi|H|\Phi\rangle + \sum_{pq} h_{pq} N[a_p^\dagger a_q] + \sum_{pq}\sum_{i}\langle pi||qi\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{pqrs}\langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$

The remaining terms now form our Φ-normal ordered Hamiltonian, $\hat{H}_N$:

$$H = \langle\Phi|H|\Phi\rangle + H_N$$

$$H_N = \sum_{pq} h_{pq} N[a_p^\dagger a_q] + \sum_{pq}\sum_{i} \langle pi||qi\rangle\, N[a_p^\dagger a_q] + \frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$

The Φ-normal ordered Hamiltonian can be further divided into 2 terms:

$$H_N = F_N + G_N$$

$$F_N = \sum_{pq} h_{pq} N[a_p^\dagger a_q] + \sum_{pq}\sum_{i} \langle pi||qi\rangle\, N[a_p^\dagger a_q]$$

$$G_N = \frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$

F_N, called the Fock operator, is an effective one-electron operator. The first term tells us about state q leaving and arriving at state p. The second term tells about state q leaving and arriving at state p *in the presence of occupied orbitals i*. It describes an effective one-body interaction that comes from a two-body operator. In other words, it contains information about two-body interactions in a mean-field manner. G_N is the usual two-electron operator.

We can re-express F_N as:

$$F_N = \sum_{pq} (h_{pq} + \sum_{i} \langle pi||qi\rangle) N[a_p^\dagger a_q]$$

$$F_N = \sum_{pq} f_{pq} N[a_p^\dagger a_q]$$

And re-express H_N as:

$$H_N = \sum_{pq} f_{pq} N[a_p^\dagger a_q] + \frac{1}{2}\sum_{pqrs} \langle pq|rs\rangle\, N[a_p^\dagger a_q^\dagger a_s a_r]$$

4 Implications of the Φ-normal ordered Hamiltonian

We have thus arrived at a Φ-normal ordered Hamiltonian:

$$H_N = H - \langle\Phi|H|\Phi\rangle$$

What have we done qualitatively? We see that the Φ-normal ordered Hamiltonian is obtained by shifting the original Hamiltonian by the expectation value in the reference determinant. In other words, it is removing the energy contribution of the reference determinant. This makes sense. In our original mapping to the particle-hole formalism, we make the reference determinant a vacuum state. Thus, the Φ-normal ordered Hamiltonian, which is in the particle-hole formalism does not have any interaction with reference determinant. In the same way that in our original formalism,

$$\langle 0|H|0\rangle = 0$$

In the particle-hole formalism,

$$\langle\Phi|H_N|\Phi\rangle = 0$$

Mathematically, the choice of the reference determinant is arbitrary. It does not matter which determinant you use in the wavefunction expansion. Practically, it is more efficient to choose a determinant that dominates the wavefunction expansion (large coefficient). If we choose our reference determinant $|\Phi\rangle$ to be the Hartree-Fock result, then shifting the Hamiltonian by the Hartree-Fock energy $E_{HF} = \langle\Phi|H|\Phi\rangle$ means we are really just defining a Hamiltonian that takes care of correlation effects.

$$H = E_{HF} + H_{correlation}$$

The Φ-normal ordered Hamiltonian is thus equal to a correlation Hamiltonian H_c:

$$H_N = H_c$$