Operator / occupation number formulation of quantum chemistry

Recall: operator approach to vibrational / vibronic problems.

operators $\hat{b}_i$, $\hat{b}_j^\dagger$ $\qquad (b_i)^\dagger = b_i^\dagger$

- satisfy commutation relations

$$[b_i, b_j] = [b_i^\dagger, b_j^\dagger] = 0$$

$$[b_i, b_j^\dagger] = \delta_{ij}$$

- states were expressed as

$$|n_i, n_j \cdots\rangle = \frac{(b_i^\dagger)^{n_i}}{\sqrt{n_i!}} \frac{(b_j^\dagger)^{n_j}}{\sqrt{n_j!}} \cdots |0\rangle$$

- Operators were expressed using powers of $b_i^\dagger$, b_j (e.g. q^4 etc.)

- $b_i |0\rangle = \langle 0 | b_i^\dagger = 0$

- Everything reduces to algebra, manipulating commutation relations.

- Wave functions & operators were expressed in terms of $b_i^\dagger$, b_i

Can we do something similar for the electronic structure problem?

Goal: reduce the problem to algebra
- suitable for computers
- We can design creative methods, not easily formulated using wave-functions.

Ingredients:

① Take ordered set of orbitals
$\{\varphi_a, \varphi_b, \varphi_c \cdots \varphi_M\}$

② Specify Slater determinant by occupation numbers 0 or 1 for each orbital

$|n_a, n_b, n_c, \cdots n_M\rangle$

$n_i = 0$ or $n_i = 1$

[Analogy: normal mode $i \leftrightarrow$ orbital a]

Example: $|1_a\, 0_b\, 1_c, \cdots 1_z \cdots\rangle$

$\equiv \frac{1}{\sqrt{N!}} |\varphi_a(1)\, \varphi_c(2) \cdots \varphi_z(N)|$

Normalized slater determinant

The sign is uniquely determined

because the ordering of orbitals in the determinant is fixed.

(3) The total # of determinants we can make is 2^M:
Every orbital can either be occupied or not → $(2 * 2 * 2 * 2 * \cdots 2)$ M times

(4) This structure includes states containing from 0 to M electrons
This space of basis-vectors is called "Fock-space"

(From Viktor Fock, Russian physicist, the same as in Hartree-Fock).

(5) We have introduced a state with 0 electrons! $|Vac\rangle = |0, 0, 0, 0, \cdots 0\rangle$

Moreover this state is normalized $\langle Vac | Vac \rangle = 1$, as are all basis states.

This indicates the structure is richer than simply "Slater-determinants"

The vacuum plays a crucial role, and is not an insignificant detail.

(6) basis-states can be written as occupation number vector $|\bar{n}\rangle$, or $|\bar{n}\rangle$
$|\bar{n}\rangle = |n_a, n_b, \cdots n_M\rangle$

(6) Similarly as for vibrations we introduce annihilation and creation operators.
I will summarize their properties here, and justify / derive later.

$$\hat{a}_p^+ \; |\vec{n}_p\rangle \rightsquigarrow |\vec{n}+1_p\rangle \cdot \text{sign}$$
or zero

$\vec{n}+1_p$: raise n_p by 1.

$$\hat{a}_p \; |\vec{n}\rangle \longrightarrow |\vec{n}-1_p\rangle \cdot \text{sign}$$
or 0

$\vec{n}-1_p$ lower n_p by 1.
all other n_i stay the same

$$\hat{a}_p \, |\text{vac}\rangle = \langle \text{vac} | a_p^+ = 0$$

$$(\hat{a}_p)^\dagger = a_p^+$$

The operators satisfy
anti commutation relations

$$\begin{cases} \hat{a}_i \hat{a}_j + \hat{a}_j \hat{a}_i = 0 \\ a_i^+ a_j^+ + a_j^+ a_i^+ = 0 \\ a_i^+ a_j + a_j a_i^+ = \delta_{ij} \end{cases}$$

This suffices to build a formal structure. I will not proceed formally but try to show what it means.

Informal introduction of annihilation and creation operators.

(See also Szabo & Ostlund)

(1) Creation operators $\hat{a}_p^+$

$$\hat{a}_p^+ \; |\varphi_a \varphi_b \cdots \varphi_z| = |\varphi_p \varphi_a \cdots \varphi_z|$$

add orbital φ_p to first position.

$$= (-)^{\Gamma_{p,\bar{n}}} |\varphi_a \varphi_b \cdots \varphi_p \cdots \varphi_z|$$

Bring it in its proper position, using the ordering of the orbitals

This requires a sign change

$\Gamma_{p,\bar{n}}$: the number of occupied orbitals <u>before</u> the location of φ_p

$$\hat{a}_p^+ \; |\bar{n}\rangle = (-)^{\Gamma_{p,\bar{n}}} \; |\bar{n}+1_p\rangle$$

if $n_p = 0$ originally.

if $n_p = 1 \longrightarrow \hat{a}_p^+ |\bar{n}\rangle = 0$, if $n_p = 1$

or: $\hat{a}_p^+ |n\rangle = (1-n_p)(-)^{\Gamma_{p,\bar{n}}} \; |\bar{n}+1_p\rangle$

The sign is needed to incorporate antisymmetry.

$\hat{a}_p^+ |\bar{n}\rangle$: Contains one more electron than $|\bar{n}\rangle$ (or is zero)

(B) : annihilation operator :

if $n_p = 0$ $\quad \hat{a}_p \, |\vec{n}\rangle = 0$

if $n_p = 1$:

$$\hat{a}_p \, | \varphi_a \cdots \varphi_p \cdots \varphi_z |$$

$$= \hat{a}_p \, (-)^{\sum_{i<p} n_i} \, | \varphi_p \varphi_a \varphi_b \cdots \varphi_z |$$

$$\equiv (-)^{\sum_{i<p} n_i} \, | \varphi_a \varphi_b \cdots \varphi_z |$$

action of $\hat{a}_p$: bring orbital to first position (sign change) then remove it from determinant.

$$\hat{a}_p \, |\vec{n}\rangle = n_p \, (-)^{\sum_{i<p} n_i} \, |\vec{n} - 1_p\rangle$$

contains one less electron than original $|\vec{n}\rangle$

From these definitions, we can deduce the anticommutation relations :

$$\hat{a}_p^\dagger \hat{a}_q^\dagger + \hat{a}_q^\dagger \hat{a}_p^\dagger = 0$$

$$\hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = 0$$

$$\hat{a}_p^\dagger \hat{a}_q + \hat{a}_q \hat{a}_p^\dagger = \delta_{pq}$$

Demonstration:

$$(\hat{a}_p^+ \hat{a}_q^+ + \hat{a}_q^+ \hat{a}_p^+) \; |\varphi_a \varphi_b \cdots \varphi_z|$$

$$= \hat{a}_p^+ \, |\varphi_q \varphi_a \varphi_b \cdots \varphi_z| + \hat{a}_q^+ \, |\varphi_p \varphi_a \cdots \varphi_z|$$

$$= |\varphi_p \varphi_q \varphi_a \cdots \varphi_z| + |\varphi_q \varphi_p \varphi_a \cdots \varphi_z|$$

$$= |\varphi_p \varphi_q \varphi_a \cdots \varphi_z| - |\varphi_p \varphi_q \varphi_a \cdots \varphi_z| = 0$$

$\Rightarrow$

$$(\hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p) \; |\varphi_a \cdots \varphi_p \cdots \varphi_q \cdots \varphi_z|$$

$$= (\hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p) \; \text{sign} \; |\varphi_p \varphi_q \varphi_a \cdots \varphi_z|$$

$$= \text{sign} \; (\hat{a}_p \hat{a}_q (-) \, |\varphi_q \varphi_p \varphi_a \cdots \varphi_z| + \hat{a}_q \hat{a}_p \, |\varphi_p \varphi_q \varphi_a \cdots \varphi_z|)$$

$$= \text{sign} \; (-|\varphi_a \varphi_b \cdots \varphi_z| + |\varphi_a \cdots \varphi_z|) = 0$$

If determinant does not contain φ_p or φ_q, every contribution is 0.

Hence $(\hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p) \; |\bar{n}\rangle = 0 \quad \forall \bar{n}$

$$\Rightarrow (\hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p) = 0$$

(I use here also that $\hat{a}_p$ is a linear operator. More discussion later).

$p \neq q$ ~~n_q, n_p~~

$$\left(\hat{a}_p^+ \hat{a}_q + \hat{a}_q \hat{a}_p^+\right) |\varphi_a \cdots \varphi_q \cdots \varphi_z| \quad \begin{cases} n_q = 1 \\ n_p = 0 \end{cases}$$

$$= \text{sign}\left(\hat{a}_p^+ \hat{a}_q + \hat{a}_q \hat{a}_p^+\right) |\varphi_q \varphi_a \cdots \varphi_z|$$

$$= \text{sign}\left(|\varphi_p \varphi_a - \varphi_z| + \hat{a}_q |\varphi_p \varphi_q \varphi_a - \varphi_z|\right)$$

$$= \text{sign}\left(|\varphi_p \varphi_a - \varphi_z| - |\varphi_p \varphi_a - \varphi_z|\right) = 0$$

if not $n_p = 1$, $n_q = 0$ then term = 0

$$\longrightarrow \quad \hat{a}_p^+ \hat{a}_q + \hat{a}_q \hat{a}_p^+ = 0 \qquad p \neq q.$$

finally $\hat{a}_p^+ \hat{a}_p + a_p a_p^+$:

$$\left(a_p^+ a_p + a_p a_p^+\right) |\varphi_a \cdots \varphi_p \cdots \varphi_z| \qquad n_p = 1$$

$$= \left(\hat{a}_p^+ \hat{a}_p + a_p a_p^+\right) \text{sign} \; |\varphi_p \varphi_a - \varphi_z|$$

$$= \hat{a}_p^+ |\varphi_a - \varphi_z| \; \text{sign} + 0 = |\varphi_p \varphi_a - \varphi_z| \; \text{sign}$$

$$= |\varphi_a - \varphi_p - \varphi_z|$$

$$\left(a_p^+ a_p + a_p a_p^+\right) |\varphi_a - \varphi_z| \qquad n_p = 0$$

$$= 0 + \hat{a}_p |\varphi_p \varphi_a - \varphi_z| = |\varphi_a - \varphi_z|$$

$$\Rightarrow \quad \left(a_p^+ a_p + a_p a_p^+\right) |\bar{n}\rangle = |\bar{n}\rangle \qquad \forall |\bar{n}\rangle$$

$$\hat{a}_p^+ \hat{a}_q + \hat{a}_p \hat{a}_p^+ = \hat{\mathbb{1}} \cdot \delta_{pq}$$

We further stipulate that the operators $\hat{a}_p$ and $\hat{a}_p^\dagger$ are linear

$$\hat{a}_p \left(\sum_n |n\rangle c_n \right) = \sum_n \left(\hat{a}_p |n\rangle \right) c_n$$

$$\hat{a}_p^\dagger \left(\sum_n |n\rangle c_n \right) = \sum_n \left(a_p^\dagger |n\rangle \right) c_n$$

Then also products, and linear combinations are linear operators

$$\sum_{p,q,r} X_{pqr} a_p^\dagger a_q a_r \sum_n |n\rangle c_n$$

$$= \sum_n \left\{ \sum_{p,q,r} X_{pqr} \left(\hat{a}_p^\dagger \hat{a}_q \hat{a}_r |n\rangle \right) \right\} c_n$$

(just evaluate one piece at a time, in whatever order, and sum it).

This is in analogy with the boson operators $b_i^\dagger$, b_j, ...

=

Every Slater determinant can be written as

$$|\bar{n}\rangle = |\psi_a \psi_b - \psi_z| = \left(\hat{a}_a^\dagger \hat{a}_b^\dagger - \hat{a}_z^\dagger \right) |\text{Vac}\rangle$$

$$= \left(\hat{a}_a^\dagger a_b^\dagger - \right) |\psi_z\rangle$$

$$= \hat{a}_a^\dagger |\psi_b - \psi_z|$$

also $\langle n| = \left(\left(a_a^\dagger a_b^\dagger \cdots \hat{a}_z^\dagger \right) |vac\rangle \right)^\dagger$

$= \langle vac| \hat{a}_z \cdots \hat{a}_b \hat{a}_a \qquad (\hat{a}_q^\dagger)^\dagger = \hat{a}_q$

take Hermitian conjugate and reverse order of operators.

$$\langle \bar{m} | a_p^\dagger | \bar{n} \rangle = \langle \bar{n} | \hat{a}_p | \bar{m} \rangle^* \qquad \forall n, m$$

$$\langle n_a \; 1_p - n_M | \hat{a}_p^\dagger | n_a - 0_p - n_M \rangle$$

$$= \langle n_a - 0_p - n_M | \hat{a}_p | n_a - 1_p - n_M \rangle = 1$$

other combinations of $n_p, m_p \to 0$.

$$(a_p)^\dagger = a_p^\dagger$$

operators are Hermitian conjugates.

The analogy with bosonic operators is complete, if we can express any operator in terms of $a_p^\dagger, \hat{a}_p$ i.e. linear combinations and powers.

This is indeed the case and moreover these expressions can be very compact.

The Hamiltonian can be expressed as:

$$H = \underbrace{\sum_{pq} \langle p|h|q\rangle \, q_p^+ a_q}_{\hat{h}} + \underbrace{\frac{1}{4} \sum_{p,q,r,s} \langle pq||rs\rangle \, (q_p^+ a_q^+ a_s a_r)}_{\hat{V}}$$

note reverse order

1) This Hamiltonian is expressed directly in terms of the one- and two-electron integrals.

2) This Hamiltonian is correct for any number of electrons

This is to be compared to

$$\hat{H} = \sum_{\lambda,\mu} |\Phi_\lambda\rangle \langle \Phi_\lambda | H | \Phi_\mu \rangle \langle \Phi_\mu |$$

$\longrightarrow$ Sum over all determinants with N electrons $\hat{H}^{(N)}$

Alternate forms:

$$\frac{1}{4} \sum_{p,q,r,s} \hat{p}^+ \hat{q}^+ \hat{s} \hat{r} \langle \hat{pq}||rs\rangle = \sum_{\substack{p<q \\ r<s}} \langle pq||rs\rangle \, \hat{p}^+ \hat{q}^+ \hat{s} \hat{r}$$

and/or

$$\frac{1}{2} \sum_{p,q,r,s} \langle pq|rs\rangle \, \hat{p}^+ \hat{q}^+ \hat{s} \hat{r}$$

Note: I am changing notation.
Once it is understood $\hat{a}_p$, $\hat{a}_p^\dagger$ refers to fermion operators, it is much more convenient to simply write $\hat{p} = \hat{a}_p$, $\hat{p}^\dagger = \hat{a}_p^\dagger$
We can even abbreviate further and simply write $p = \hat{p}$, $q^\dagger = \hat{q}^\dagger$

Let us consider alternatives:

$$\frac{1}{4} \sum_{p,q,r,s} \langle pq||rs\rangle\, p^\dagger q^\dagger s r$$

$$= \frac{1}{4} \sum_{p,q,r,s} \left(\langle pq|rs\rangle - \langle pq|sr\rangle \right) p^\dagger q^\dagger s r$$

$$= \frac{1}{4} \sum_{p,q,r,s} \langle pq|rs\rangle\, p^\dagger q^\dagger s r$$

$$- \frac{1}{4} \sum_{p,q,r,s} \langle pq|sr\rangle\, p^\dagger q^\dagger s r$$

↷ flip → − sign

$$= \frac{1}{4} \sum_{p,q,r,s} \langle pq|rs\rangle\, p^\dagger q^\dagger s r$$

$$+ \frac{1}{4} \sum_{p,q,r,s} \langle pq|sr\rangle\, p^\dagger q^\dagger r s$$

$r \to r s$, $s \to s r$

(rename $r \leftrightarrow s$, $s \to r$ allowing summation)

$$= \frac{1}{2} \sum_{p,q,r,s} \langle pq|rs\rangle\, p^\dagger q^\dagger s r$$

Let us demonstrate (argue) that Hamiltonian in second quantization is indeed correct → yields same matrix-elements as original Hamiltonian. (Slater rules)

Use: $\left[\sum_{p,q}^{4} h_{pq}\, p^+ q,\ r^+\right] = \left[\hat{h}, r^+\right] = \dots$

~~$= h_{pq}\,(p^+ \quad q\ r$~~

$$\hat{h}\, r^+ = \sum_{p,q} h_{pq}\ p^+ q\ r^+ = \sum_{p,q} h_{pq}\ p^+ \{q, r^+\}$$

$$- \sum_{p,q} h_{pq}\ p^+ r^+ q = \sum_{p,q} h_{pq}\left(p^+ \delta_{qr} + r^+ p^+ q\right)$$

$$= \sum_{p} h_{pr}\, p^+ + r^+ \hat{h}$$

or $$\left[\hat{h}, r^+\right] = \sum_{p} h_{pr}\, p^+ + \cancel{r^+ \hat{1}} - r^+ \hat{h}$$

Now evaluate matrix elements

$$\langle \mathrm{vac} | (\hat{z} \cdots \hat{b}\,\hat{a})\ \hat{h}\ \hat{a}^+ \hat{b}^+ \cdots \hat{z}^+ | \mathrm{vac} \rangle$$

$$= \langle \mathrm{Vac} | (\hat{z} \cdots \hat{b}\,\hat{a})\ \left[\hat{h}, a^+\right] \hat{b}^+ \cdots \hat{z}^+ | \mathrm{vac} \rangle$$
$$+ \langle \mathrm{vac} | (\hat{z} \cdots \hat{b}\,\hat{a})\ a^+ \left[\hat{h}, b^+\right] \cdots z^+ | \mathrm{vac} \rangle$$
$$+ \cdots \langle \mathrm{vac} | (\hat{z} \cdots \hat{a})\ a^+ b^+ \cdots \left[h, z^+\right] | \mathrm{vac} \rangle$$
$$+ \langle \mathrm{vac} | (z \cdots a)\ (a^+ b^+ \cdots z^+)\ \hat{h} | \mathrm{vac} \rangle$$

in order to give non-zero matrix-elements

$[h, a^\dagger]\, b^\dagger \cdots z^\dagger |vac\rangle \rightarrow \langle ab\cdots z|$ determinant in bra.

hence only surviving contribution

$[\hat{h}, a^\dagger] = \sum_p h_{pa}\, p^\dagger$ $\boxed{p = a}$ only contribution

Same argument for $[\hat{h}, b^\dagger], \cdots [\hat{h}, z^\dagger]$

$\rightarrow$ contribution $h_{aa} + h_{bb} + \cdots h_{zz}$

final contribution:

$$a^\dagger b^\dagger \cdots z^\dagger\, h_{pq}\, \hat{p}^\dagger \hat{q}\, |vac\rangle = 0$$

because $\hat{q}\, |vac\rangle = 0$

Hence: $\langle k | h | k \rangle = \sum_{a \text{ in } k} h_{aa}$

~~Same~~ is correct result.

I used a useful trick

$$\hat{h}\, \hat{o}_1\, \hat{o}_2\, \hat{o}_3 = [\hat{h}, \hat{o}_1]\, \hat{o}_2\, \hat{o}_3 + \hat{o}_1 h_1\, \hat{o}_2\, \hat{o}_3$$

$$= [\hat{h}, o_1]\, \hat{o}_2\, \hat{o}_3 + \hat{o}_1 [\hat{h}, \hat{o}_2]\, \hat{o}_3 + \hat{o}_1\, \hat{o}_2\, [\hat{h}, \hat{o}_3] + \cdots \hat{o}_1\, \hat{o}_2\, \hat{o}_3\, \hat{h}$$

This is true for any string of operators

~~$[A, BCD\cdots] = [A, B]\, \hat{C}\, \hat{D}\cdots + \hat{A}\, [A, \hat{B}]\, \hat{C}\, \hat{D}\cdots$~~

~~$+ \hat{A}\, \hat{B}$~~

$$[\hat{O}, \hat{A}\hat{B}\hat{C}\cdots] = [\hat{O},\hat{A}]\hat{B}\hat{C}\cdots + \hat{A}[\hat{O},\hat{B}]\hat{C}\cdots + \hat{A}\hat{B}[\hat{O},\hat{C}]\cdots + \hat{A}\hat{B}\hat{C}[\hat{O},\hat{D}]\cdots$$

~~$+ \hat{A}\hat{B}\hat{C}\cdots\hat{O}$~~

$=$ Let us also do off-diagonal one-electron matrix element:

$$\langle \text{Vac}|(z\cdots bp)\,\hat{h}\,(a^+ b^+ \cdots z^+)|\text{Vac}\rangle$$

$$= \langle \text{Vac}|(z\cdots bp)\,\underset{p^+\ a}{[h,a^+]}(b^+\cdots z^+)|\text{Vac}\rangle$$

$$+ \langle \text{Vac}|(z\cdots bp)\,a^+[h,b^+]\cdots|\text{Vac}\rangle + \cdots.$$

the leste term and all others vanish because orbital a (from a^+) is not among $\langle \text{Vac}|\, z\cdots bp$

$\longrightarrow$ only the first term contributes

$[h,a^+] = \sum_r h_{ra}\, r^+ \longrightarrow r = p$, has to match orbital p

$\longrightarrow \langle k'|\hat{h}|k\rangle = h_{pa}$, as before.

Note: We do not need to worry about permutations, or factors of $N!$ annihilation and creation operators take care of it all.

Let us do one more matrix-element, involving $\hat{V} = \frac{1}{4} \sum_{pqrs} \langle pq||rs\rangle p^\dagger q^\dagger s r$

Consider $\langle k' | V | k \rangle$ (the easiest)

$$\langle vac | \left(z \cdots c \; \cancel{\text{ut}} \; \sum \frac{1}{4} p^\dagger q^\dagger s r \langle pq||rs\rangle \right) (a^\dagger b^\dagger c^\dagger \cdots z^\dagger | vac\rangle$$

→ only contributions:

$s=b$, $r=a$,	$p=t$	$q=u$	$\langle tu\|\|ab\rangle \frac{1}{4}$
$s=a$, $r=b$	$p=t$,	$q=u$	$-\langle tu\|\|ba\rangle \frac{1}{4}$
$s=b$, $r=a$,	$p=u$,	$q=t$	$-\langle ut\|\|ab\rangle \frac{1}{4}$
$s=a$, $r=b$	$p=t$,	$q=u$	$+\langle ut\|\|ba\rangle 1/4$

~~Then~~ V must involve the orbitals that are different, otherwise mismatch.

Let us consider first contribution

$$ut \; t^\dagger u^\dagger \; b \; a \; a^\dagger b^\dagger$$
$$= ut \; t^\dagger u^\dagger \; b \; \{a, a^\dagger\} \; b^\dagger - ut \; t^\dagger u^\dagger \; b \; a^\dagger a \; b^\dagger$$

zero ← $\hat{a}|vac\rangle = 0$

$\hat{a}, (b^\dagger c^\dagger \cdots z^\dagger) = (b^\dagger c^\dagger \cdots z^\dagger \; a)$ (no matches.)

→ $ut \; t^\dagger u^\dagger \; \{b, b^\dagger\} - ut \; t^\dagger u^\dagger \; b^\dagger \; b \cdots |vac\rangle$

↓

other matches without sign change.

→ the first term has + sign.

For the other terms we can put them in matching order, by permuting

e.g. $u\,t\;\; t^+u^+\;a\,b\;\; a^+b^+ \cdot \langle tu||ba\rangle$

$= - \overbrace{u\,t\;\; t^+u^+}\;\overbrace{b\,a\;\; a^+b^+}\;\langle tu||ba\rangle$

$\smile$ flip

$= - \langle tu||ba\rangle = + \langle tu||ab\rangle$

The same is true for all other contributions

$\frac{1}{4}\left(\langle tu||ab\rangle - \langle tu||ba\rangle - \langle ut||ab\rangle + \langle ut||ba\rangle\right)$

$= +1\;\langle tu||ab\rangle$

$= \cancel{ab\,tu}\;\langle tu\;c\,d\,\ldots z|\;\hat{r}_{12}\;|ab\;c\ldots z\rangle$

using Slater rules.

Let us develop a little further the device where we indicate which indices are the same.

$\langle pq||rs\rangle \quad u\,t\;\; p^+q^+\;s\,r\;\; a^+b^+ \;\rightarrow\; \langle \cancel{ut}||ab\rangle$ (tu)

$\langle pq||rs\rangle \quad u\,t\;\; p^+q^+\;s\,r\;\; a^+b^+ \;\rightarrow\; -\langle \cancel{ut}||ba\rangle$ (tu)

$\langle pq||rs\rangle \quad u\,t\;\; p^+q^+\;s\,r\;\; a^+b^+ \;\rightarrow\; -\langle \cancel{tu}||ab\rangle$ (ut)

$\langle pq||rs\rangle \quad u\,t\;\; p^+q^+\;s\,r\;\; a^+b^+ \;\rightarrow\; +\langle tu||ba\rangle$

$\cancel{\langle ut||ba\rangle = \langle tu||ab\rangle}$

$+4\,\langle ut||ab\rangle$

Using lines to indicate the matching indices, we can obtain the indices in the

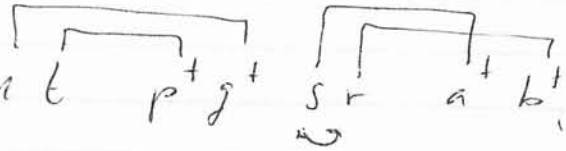
i) 2-electron integrals

ii) the sign of the expression from the number of intersections of the lines

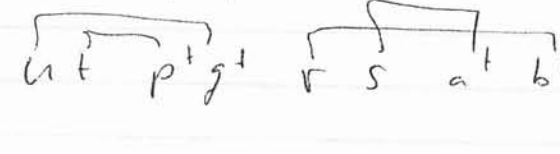
$$(-)^{\#\ \text{crossings}} = \text{sign}$$

= number of permutations in V operator to undo the sign change

e.g. $u\,t\;\; p^\dagger q^\dagger\;\; s\,r\;\; a^\dagger\; b^\dagger$



$$= - \; u\,t\;\; p^\dagger q^\dagger\;\; r\,s\;\; a^\dagger\; b^\dagger$$



$$= - \; u\,t\;\; p^\dagger q^\dagger\;\; r\,s\;\; a^\dagger\; b^\dagger$$

(it does not matter how you draw the lines.)

We will use this tool to perform contractions, or evaluate matrix-elements in what is to follow.

Summary:

The Hamiltonian in second quantization reads

$$\hat{H} = \sum_{p,q} h_{pq}\, \hat{p}^{+}\hat{q} + \frac{1}{4}\sum_{\substack{p,q\\r,s}} \langle pq||rs\rangle\, \hat{p}^{+}\hat{q}^{+}\hat{s}\hat{r}$$

Determinants can be represented as

$$|\Delta\rangle = \hat{a}^{+}\hat{b}^{+}\cdots\hat{i}^{+}\,|\,vac\rangle$$

Then matrix-elements $\langle K|\hat{H}|L\rangle$ can be evaluated using the anticommutation relations. The results agree with the Slater rules.

The Hamiltonian applies to systems with any number of electrons.

There is a very rich field of application of second quantized methods in quantum chemistry. Current developments in wave function based quantum chemistry, and even density matrix based quantum chemistry, invariably are based on this operator approach.

Density functional theory is very different, and second quantization hardly plays any role there.

I will discuss some fairly elementary applications.

The ground state of a system (closed shell molecule around equilibrium bond length) is often qualitatively well described by single determinant, in which the orbitals are optimized.

That single determinant which minimizes the energy $\langle \Phi | \hat{H} | \Phi \rangle$ is called the Hartree-Fock (HF) determinant and HF energy.
This is the topic in the next chapter in S&O. (Chapter 3)

Let us assume we have solved this problem, and the HF state is represented as

$$a^+ b^+ \cdots c^+ \, | \text{vac} \rangle = | \text{HF} \rangle$$

→ occupied orbitals in $|\text{HF}\rangle$ are labelled a, b, c, d.

The remaining (orthonormal) orbitals, so-called virtual orbitals are labelled $r, s, t, u, \ldots$

Following S&O unspecified orbitals have labels $i, j, k, l, \ldots$

Excitations out of the HF determinant are represented as

$\hat{r}^+\hat{a} \mid HF\rangle$: take out orbital 'a' put in orbital 'r' (virtual).

This is a single excitation.

a general single excited state can be expressed as the linear combination

$$\sum_{r,a} \hat{r}^+\hat{a} \mid HF\rangle \; C_a^r$$

C_{ra} : coefficients

Likewise double excitations are written as

$$\sum_{\substack{r<s \\ a<b}} r^+ s^+ \hat{b}\hat{a} \mid HF\rangle \; C_{ab}^{rs}$$

$$= \sum_{\substack{r<s \\ a<b}} \hat{r}^+\hat{a}\,\hat{s}^+\hat{b} \mid HF\rangle \; C_{ab}^{rs}$$

restricting the summation ~~restricts~~ includes only unique determinants

Improved ground includes combination of excited determinants

Using the power of second quantization, we can look at states with a different number of electrons, for example

The simplest parameterization of ionized states would be

$$\sum_a \hat{a} |HF\rangle C_a$$

or, in next approximation:

$$\sum_a \hat{a} |HF\rangle C_a + \sum_{\substack{a<b \\ r}} r^\dagger b \hat{a} |HF\rangle C_{ab}^r$$

Similarly for states with 1 more electron (electron attachment)

$$\sum_r r^\dagger |HF\rangle C_r$$

or, more accurately:

$$\sum_r r^\dagger |HF\rangle C_r + \sum_{r,s,a} r^\dagger s^\dagger a |HF\rangle C_{rsa}^{rs}$$

The idea is:
include small number of substitutions or deletions out of the Hartree Fock state to parameterize excitations / ionizations

Then use the variational principle:
⟶ obtain matrix-elements
$\langle \Phi_\lambda | H | \Phi_\mu \rangle$
over limited set of determinants and diagonalize.

How to calculate matrix-elements?

⇒ Use techniques of second quantization!

Time to work through some examples:

(A) ionization energies:

$$|\Psi_\lambda\rangle = \sum_a \hat{a} |HF\rangle \, C_{a,\lambda}$$

→ Hamiltonian elements

$\langle HF | \hat{b}^+ \hat{H} \hat{a} | HF \rangle$ a,b: occupied orb's in $|HF\rangle$.

Strategy: Move operators $\hat{a}$, $\hat{b}^+$ using anti commutation rules, such that $\hat{a}$ acts on bra:

$$\langle HF | a = (a^+ |HF\rangle)^+ = 0$$

$\hat{b}^+$ acts on ket:

$$b^+ |HF\rangle = 0$$

(I cannot create occupied orbital twice → 0).

This is reflected as writing expression in normal order (Compare vibrational) → operators $\hat{b}^+$, $\hat{r}$ to right, operators a, r^+ to left

r: virtual orbital: $\hat{r} |HF\rangle = 0$

$\langle HF | \hat{r}^+ = 0$

Let us work it out for one-electron elements

$$\sum_{ij} h_{ij} \langle HF | b^\dagger i^\dagger j \, a | HF \rangle$$

$$= \sum_{ij} h_{ij} (-) \langle HF | b^\dagger i^\dagger a j | HF \rangle$$

$$= \sum_{ij} h_{ij} \Big[(-) \delta_{ia} \langle HF | b^\dagger j | HF \rangle + \langle HF | b^\dagger a \, i^\dagger j | HF \rangle$$

$$= \sum_{ij} h_{ij} \Big[(-) \delta_{ia} \delta_{jb} + \delta_{ab} \langle HF | i^\dagger j | HF \rangle$$

$$= -h_{ab} + \delta_{ab} \langle HF | \hat{h} | HF \rangle$$

$$= -h_{ab} + \delta_{ab} \sum_c h_{cc}$$

Let us also do it in an alternative way, drawing lines to indicate which lines are paired:

$$\sum_{ij} h_{ij} \Big[\langle HF | b^\dagger \overbrace{i^\dagger j} a | HF \rangle + \langle HF | b^\dagger \overbrace{i^\dagger j} | a | HF \Big]$$

→ if $\overbrace{i^\dagger j}$ is paired it means they have to be occupied labels:

$$\sum_{ij} h_{ij} \langle HF | i^\dagger j | HF \rangle = \sum_c h_{cc}$$

Hence 'line' expression reduces to

$$- h_{ab} + \delta_{ab} \sum_c h_{cc} \quad \text{as before.}$$