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② Operators, matrix elements, molecular integrals

i) Integrals

1-electron operator : $-\frac{1}{2}\nabla_i^2$, $-\sum_I \frac{Z_I}{r_{iI}}$,

2-electron operator : $\frac{1}{r_{ij}}$

(0-electron operator : $\sum_{I<J} \frac{Z_I Z_J}{r_{IJ}}$)

Definition : 1-electron integrals

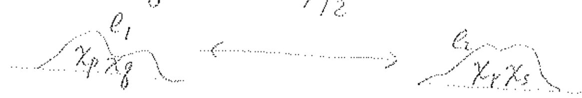
$$\underset{\text{chemists'}}{(p|h|q)} = \underset{\text{physicists'}}{\langle p|h|q\rangle} = \int \chi_p^*(\mathbf{x})\, \hat{h}(\mathbf{x})\, \chi_q(\mathbf{x})\, d\mathbf{x} = \underset{\text{tensor}}{h^p_q}$$

$$(p|h|q) = (q|h|p)^*$$

Definition : 2-electron integrals

chemists'

$$\underset{1^*\ 1\ \ 2^*\ 2}{(pq|rs)} = \int \chi_p^*(\mathbf{x}_1)\, \chi_q(\mathbf{x}_1)\, \frac{1}{r_{12}}\, \chi_r^*(\mathbf{x}_2)\, \chi_s(\mathbf{x}_2)\, d\mathbf{x}_1 d\mathbf{x}_2$$



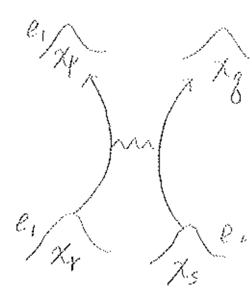
Coulomb repulsion between charge densities (suitable for HF, DFT?)

$$(pq|rs) = (rs|pq) = (qp|sr)^* = (sr|qp)^*$$

$$\underset{1^*\ 1\ \ 2^*\ 2}{(pq||rs)} = (pq|rs) - (ps|rq) = v^{\overset{1^*\,2^*}{pr}}_{\underset{1\ \ 2}{qs}} \quad \text{tensor}$$

$$(pq||rs) = -(ps||qr) = -(rq||ps) = (rs||pq)$$

$$v^{pr}_{qs} = -v^{pr}_{sq} = -v^{rp}_{qs} = v^{rp}_{sq}$$



Coulomb int. causes e. pair to be scattered into another pair.

physicists'

$$\underset{1^*\ 2^*\ \ 1\ 2}{\langle pq|rs\rangle} = \int \chi_p^*(\mathbf{x}_1)\, \chi_q^*(\mathbf{x}_2)\, \frac{1}{r_{12}}\, \chi_r(\mathbf{x}_1)\, \chi_s(\mathbf{x}_2)\, d\mathbf{x}_1 d\mathbf{x}_2$$

(suitable for correlation?)

$$\underset{1^*\ 2^*\ \ 1\ 2}{\langle pq||rs\rangle} = \langle pq|rs\rangle - \langle pq|sr\rangle = v^{\overset{1^*\,2^*}{pq}}_{\underset{1\ \ 2}{rs}} \qquad (\langle pp||rs\rangle = \langle pq||rr\rangle = 0)$$

$$\langle pq||rs\rangle = -\langle pq||sr\rangle = -\langle qp||rs\rangle = \langle qp||sr\rangle$$

ii) Slater-Condon rules — unweildy!

General 1-electron operator $\hat{O}_1 = \sum_i \hat{h}_i = \left(\sum_i\right) -\frac{1}{2}\nabla_i^2 - \left(\sum_i\right)\sum_I \frac{Z_I}{r_{iI}}$

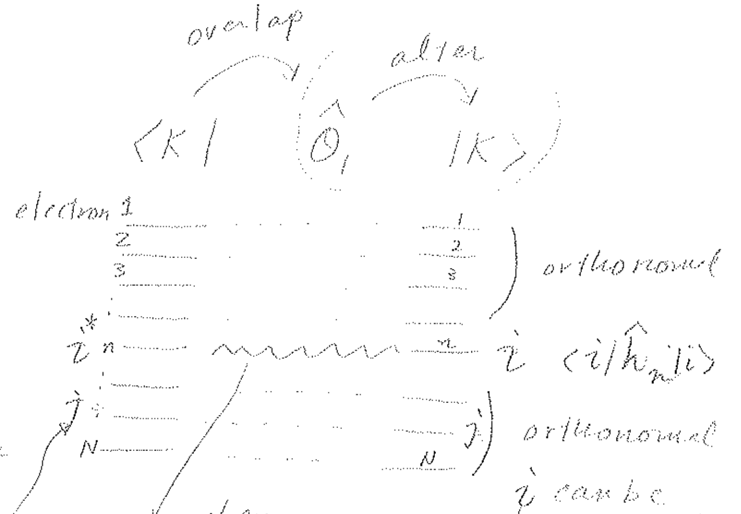
It can act on all electrons

General 2-electron operator $\hat{O}_2$

Here we specify $\hat{O}_2 = \sum_{i<j} \frac{1}{r_{ij}}$, it acts on all distinct pairs

(A) 0-electron difference

$$\langle K|\hat{O}_1|K\rangle = \sum_i \langle i|\hat{h}|i\rangle$$

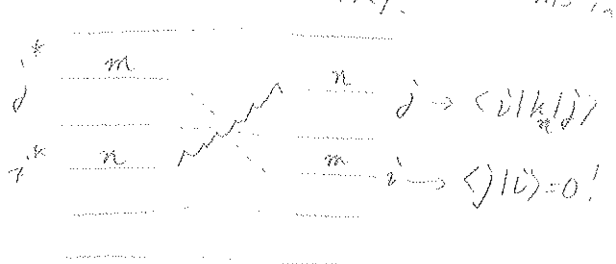


First, let us focus on one orbital product α in $N!$ terms in the determinant $|K\rangle$. Each orbital has certain electron like this

then Let us focus on the effect of $\hat{h}(x_n)$. $\hat{h}(x_n)$ can act on the spin-orbital χ_i which is occupied by e_n and alter it, say $\hat{h}(x_n)\chi_i(x_n)$. This can yield nonzero integral with any $\chi_j^*(x_n)$, $\langle j|h|i\rangle$. However, all $i \neq j$ partnering cause the remaing orbitals to have mismatch. If χ_j is occupied by electron m in the product α, electron m must occupy orbital other than χ_j^* (already occupied by electron n) in β, say χ_k^*. Then

$$\langle \chi_k(x_m)|\chi_j(x_m)\rangle = 0 \text{ occurs.}$$

Coming from some product β among $N!$ terms in $\langle K|$.



The only way the overall integral survives is $\alpha = \beta$ and gives $\frac{\langle i|h|i\rangle}{N!}$

Other $x_n \longrightarrow \sum \frac{\langle i|h|i\rangle}{N!}$

Other $\alpha \longrightarrow \sum_i \langle i|h|i\rangle$

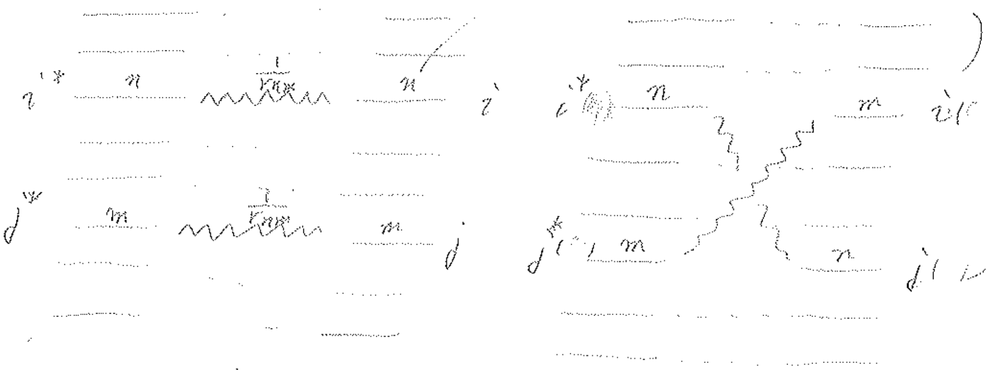
$$\langle K|\hat{O}_2|K\rangle = \sum_{i<j}\langle ij||ij\rangle = \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle$$

$$\langle K| \overset{\text{overlap}}{} \hat{O}_i \overset{\text{alter}}{} |K\rangle \to \sum_{n<m}\frac{1}{r_{nm}}$$

electron #

orthonormal

$\langle ij|ij\rangle$
$n^* m^* n\, m$



$1^* 2^* | 12$

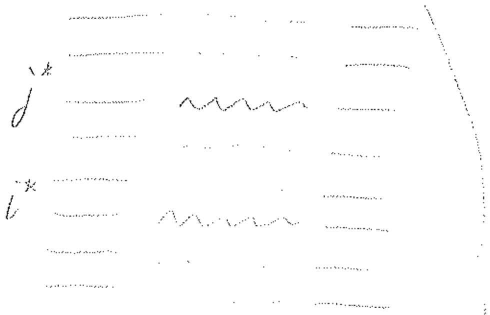
$-\langle ij|ji\rangle$

because e_n and e_m must be swapped to make the match;

same

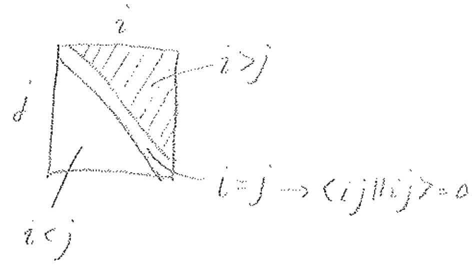
double counting

$\langle ji|ji\rangle$



$$\frac{1}{2}\sum_i \sum_{\substack{j \\ (j\neq i)}} \langle ij|ij\rangle - \frac{1}{2}\sum_i \sum_{\substack{j \\ (j\neq i)}} \langle ij|ji\rangle = \frac{1}{2}\sum_{i,j}\langle ij||ij\rangle$$

(note: $\langle ii||ii\rangle = 0$)

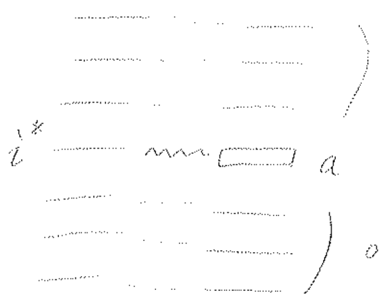


(B) One-electron difference

$$|K\rangle = |\cdots i \cdots\rangle$$
$$|L\rangle = |\cdots a \cdots\rangle$$

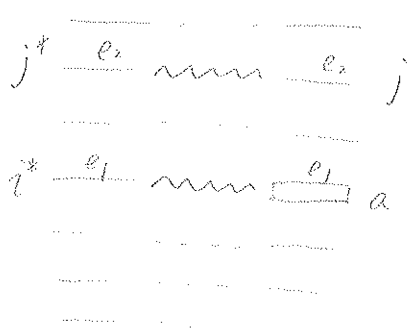
$$\langle K|\hat{O}_1|L\rangle = \langle i|h|a\rangle$$

$$\langle K| \quad \hat{O}_1 \quad |L\rangle$$



$$\langle K|\hat{O}_2|L\rangle = \sum_j \langle ij||aj\rangle$$

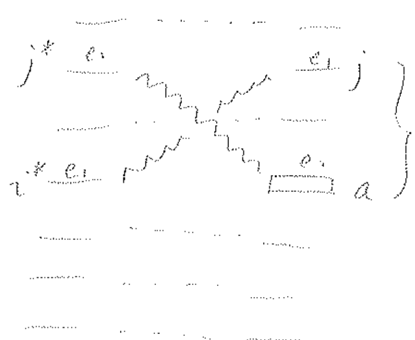
$$\langle K| \quad \hat{O}_2 \quad |L\rangle$$



$\langle i\, j\, |a\, j\rangle$
$1^*\, 2^*\;\; 1\;\, 2$

j can be any thing other than i
$\rightarrow \sum_j$

$$\langle K| \quad \hat{O}_2 \quad |L\rangle$$



$-\langle i\, j\, |j\, a\rangle$
$1^*\, 2^*\;\; 1\;\, 2$

$$\sum_{j \neq i} \langle ij|aj\rangle - \sum_{j\neq i}\langle ij|ja\rangle = \sum_j \langle ij||aj\rangle$$

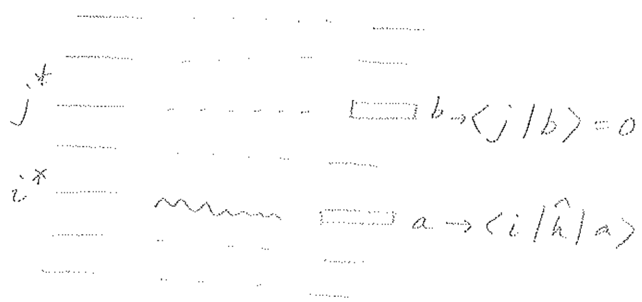
(note: $\langle ii||ai\rangle = 0$)

Ⓒ Two-electron difference

$$|K\rangle = |\cdots i \cdots j \cdots\rangle$$
$$|L\rangle = |\cdots a \cdots b \cdots\rangle$$

$$\langle K|\hat{O}_1|L\rangle = 0$$

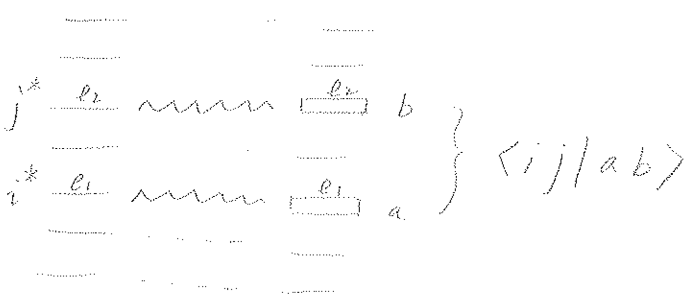
$\langle K| \quad \hat{O}_1 \quad |L\rangle$



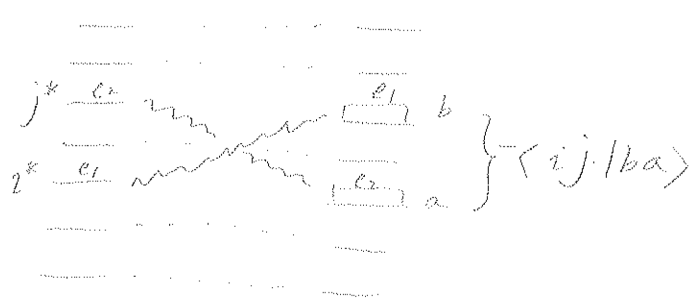
there's always at least one mismatch with zero overlap

$$\langle K|\hat{O}_2|L\rangle = \langle ij||ab\rangle$$

$\langle K| \quad \hat{O}_2 \quad |L\rangle$



$\langle K| \quad \hat{O}_2 \quad |L\rangle$



$$\langle ij|ab\rangle - \langle ij|ba\rangle = \langle ij||ab\rangle$$

Ⓓ Three- or more electron difference

$$|K\rangle = |\cdots i \cdots j \cdots k \cdots\rangle$$
$$|L\rangle = |\cdots a \cdots b \cdots c \cdots\rangle \qquad \langle K|\hat{O}_1|L\rangle = \langle K|\hat{O}_2|L\rangle = 0$$

$$\hat{H} = \underbrace{\sum_i \underbrace{\left(-\frac{1}{2}\nabla_i^2 - \sum_I \frac{Z_I}{r_{iI}}\right)}_{\hat{h}(i)}}_{\hat{O}_1} + \underbrace{\sum_{i<j} \frac{1}{r_{ij}}}_{\hat{O}_2}$$

Example 1.

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

$$= \langle \Phi_0 | \hat{O}_1 | \Phi_0 \rangle + \langle \Phi_0 | \hat{O}_2 | \Phi_0 \rangle$$

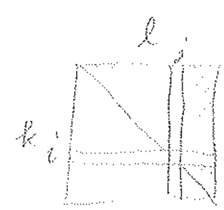
$$= \sum_i \langle i | \hat{h} | i \rangle + \frac{1}{2} \sum_{i,j} \langle ij || ij \rangle$$

Example 2.

remove an electron from χ_j
add " to χ_a

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

$$= \langle \Phi_i^a | \hat{O}_1 | \Phi_j^b \rangle + \langle \Phi_i^a | \hat{O}_2 | \Phi_j^b \rangle$$



if $a=b,\ i=j$

$$\sum_{k \neq i} \langle k | \hat{h} | k \rangle + \langle a | \hat{h} | a \rangle$$

if $a=b,\ i \neq j$

$-\langle j | \hat{h} | i \rangle$ (note j is filled in Φ_i^a)

if $a \neq b,\ i=j$

$$\langle a | \hat{h} | b \rangle$$

one swap to align orbitals $\rightarrow \langle j | h | i \rangle$

if $a \neq b,\ i \neq j$

$$0$$

if $a=b,\ i=j$

$$\frac{1}{2}\Big(\sum_{k,l} \langle kl || kl \rangle - \sum_l \langle il || il \rangle - \sum_k \langle kj || kj \rangle + \sum_l \langle al || al \rangle + \sum_k \langle kb || kb \rangle\Big)$$

if $a=b,\ i \neq j$

$$-\sum_l \langle jl || il \rangle - \langle ja || ia \rangle$$

if $a \neq b,\ i=j$

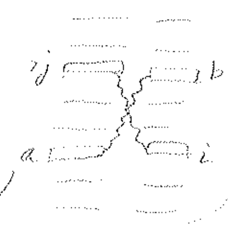
$$\sum_{l (\neq i)} \langle al || bl \rangle$$

these exceptions are absorbed here making $a \neq b \rightarrow a, b$; $i \neq j \rightarrow i, j$

Fock operator
$$\langle p | \hat{f} | q \rangle = \langle p | \hat{h} | q \rangle + \sum_k \langle pk || qk \rangle$$

if $a \neq b,\ i \neq j$

$$-\langle aj || bi \rangle$$



$$\langle a | \hat{f} | b \rangle \delta_{ij}$$

$$\langle \Phi_i^a | \hat{H} | \Phi_j^b \rangle = \overbrace{E_{HF}}^{\delta_{ab}\delta_{ij}} + \langle a | h | b \rangle \delta_{ij} + \sum_l \langle al || bl \rangle \delta_{ij} - \langle j | h | i \rangle \delta_{ab} - \sum_l \langle jl || il \rangle \delta_{ab} - \langle aj || bi \rangle$$

$$\langle j | f | i \rangle \delta_{ab}$$

$$= E_{HF} + \langle a | f | b \rangle^{\delta_{ij}} - \langle j | f | i \rangle^{\delta_{ab}} - \langle aj || bi \rangle$$