Evaluation of $\langle HF | b^+ \hat{H} \{ a | HF \rangle$ continued.

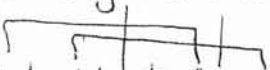
We saw: $\langle HF | b^+ \hat{h} \{ a | HF \rangle = -h_{ab} + \sum_c h_{cc}$

Let us next evaluate $\hat{V}$ contribution:

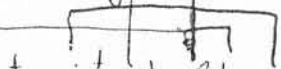
$$\frac{1}{4} \sum_{i,j,k,l} \langle HF | b^+ i^+ j^+ l k a | HF \rangle \langle ij||kl \rangle$$

$$= \frac{1}{4} \sum_{i,j,k,l} \langle ij||kl \rangle \Big[\langle HF | b^+ i^+ j^+ l k a | HF \rangle$$

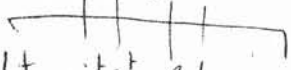
$$+ \langle HF | b^+ i^+ j^+ l k a | HF \rangle$$



$$\langle HF | b^+ i^+ j^+ l k a | HF \rangle$$



$$\langle HF | b^+ i^+ j^+ l k a | HF \rangle$$



$$+ \langle HF | b^+ i^+ j^+ l k a | HF \rangle \quad (4 \text{ contr.})$$

$$= \frac{1}{4} \sum_c \langle ca||cb \rangle \quad (-)$$

$$+ \frac{1}{4} \sum_c \langle ca||bc \rangle \quad (+)$$

$$+ \frac{1}{4} \sum_c \langle ac||cb \rangle \quad (+)$$

$$+ \frac{1}{4} \sum_c \langle ac||bc \rangle \quad (-)$$

$$\rightarrow -\sum_c \langle ac||bc \rangle$$

$$+ \delta_{ab} \langle HF | \hat{V} | HF \rangle$$

Hence in total we have obtained

$$\langle MF | b^+ \hat{H} a | MF \rangle$$

$$= - h_{ab} - \sum_c \langle ac || bc \rangle + \langle MF | \hat{H} | MF \rangle$$

Define so-called Fock matrix

$$- f_{ab} = - h_{ab} - \sum_{c \in |MF)} \langle ac || bc \rangle$$

then $\langle MF | b^+ \hat{H} a | MF \rangle$

$$= - f_{ab} + E_{HF} \delta_{ab}$$

diagonalize f_{ab} (over occupied orbitals)

$$\sum_b f_{ab} C_{b\lambda} = \varepsilon_\lambda C_{a,\lambda}$$

→ "orbital eigenvalues" are approximations to ionization energies

$$E_{IP,\lambda} - E_{HF} \approx - \varepsilon_\lambda$$

$$- \varepsilon_\lambda > 0 \quad (E_{HF} < E_{IP})$$

ε_λ, eigenvalues of $\hat{f}$ for occupied orbitals are negative (printed in Gaussian ...)

Let us also consider electron attachment states with one more electron

$$\Psi_\mu = \sum_r \hat{r}^+ |HF\rangle C_{r,\mu}$$

r: virtual orbital, not occupied in $|HF\rangle$

$\Rightarrow$ evaluate matrix-elements

$\langle HF| \hat{s} \hat{H} \hat{r}^+ |HF\rangle$ r, s virtual

$\Rightarrow$ use 'line'-algorithm: $\hat{h}$ first

$$\sum_{ij} h_{ij} \left[\langle HF| \hat{r} \hat{i}^+ \hat{j} \hat{s}^+ |HF\rangle + \langle HF| \hat{r} \hat{i}^+ \hat{j} \hat{s}^+ |HF\rangle \right]$$

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

$$= h_{rs} + \sum_c h_{cc}$$

$$\frac{1}{4} \sum_{i,j,k,l} \langle ij||kl\rangle \Big[\langle HF| \hat{r} \hat{i}^+ \hat{j}^+ \hat{l} \hat{k} \hat{s}^+ |HF\rangle \to \sum_c \langle rc||sc\rangle$$

$$+ \langle HF| \hat{r} \hat{i}^+ \hat{j}^+ \hat{l} \hat{k} \hat{s}^+ |HF\rangle \to -\langle cr||sc\rangle$$

$$+ \langle HF| \hat{r} \hat{i}^+ \hat{j}^+ \hat{l} \hat{k} \hat{s}^+ |HF\rangle \to -\langle rc||cs\rangle$$

$$+ \langle HF| \hat{r} \hat{i}^+ \hat{j}^+ \hat{l} \hat{k} \hat{s}^+ |HF\rangle \quad \langle cr||cs\rangle$$

$$+ \langle HF| \hat{r} \hat{i}^+ \hat{j}^+ \hat{l} \hat{k} \hat{s}^+ |HF\rangle \quad \delta_{rs} \langle \hat{V} \rangle_{HF}$$

In total the 4 permutations of $\frac{1}{4}\langle rc||sc\rangle$ add up to $+1\langle rc||sc\rangle$

hence $\langle HF|r\,H\,s^+|HF\rangle$

$$= h_{rs} + \sum_c \langle rc||sc\rangle + \delta_{rs}\langle HF|\hat{H}|HF\rangle$$

$$\equiv f_{rs} + \delta_{rs} E_{HF}$$

$\rightarrow$ diagonalize f_{rs} over virtual labels $f_{rs} C_{s\lambda} = \varepsilon_\lambda C_{r\lambda}$

$\Rightarrow$ ε_λ virtual orbital energies

$$\left(E_{(N+1),\lambda} - E_{HF}\right) = \varepsilon_\lambda$$

$\varepsilon_\lambda > 0$ typically.

This would mean one cannot bind an extra electron, and these energies are artifacts of finite basis calculation.
Only $\varepsilon_\lambda < 0$ would have solid physical meaning.

The ~~energies~~ Ionization energies, eigenvalues of the Fock matrix are often reasonable (errors of about 1 eV out of ~10 eV)

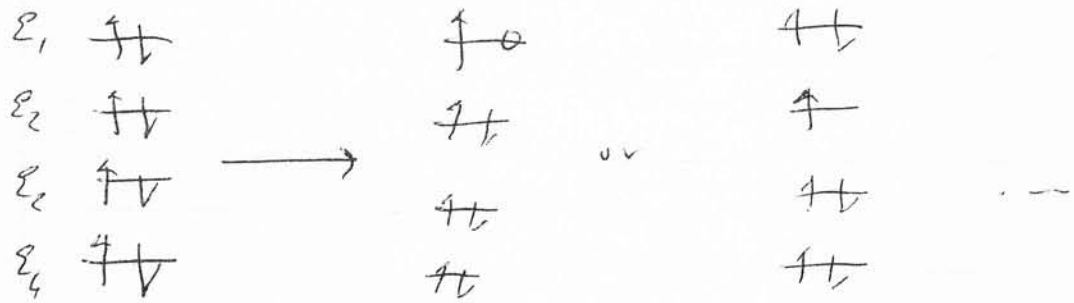
This is called Koopmans' theorem.

It is perfectly fine to define the orbitals occupied in (HF) as the so-called canonical orbitals = eigenvectors of the Fock matrix

If I make linear combinations of the columns in a determinant, the determinant stays the same.

⇒ orbitals are somewhat arbitrary. Only the determinant matters.
(See later for more discussion)
(also see lecture notes --)

If we choose the orbitals as eigenvectors of the Fock matrix we get a simple picture



$\Delta E = -\varepsilon_1$ $\Delta E = -\varepsilon_2$

$\hat{a}_1 |HF\rangle$ $\hat{a}_2 |HF\rangle$

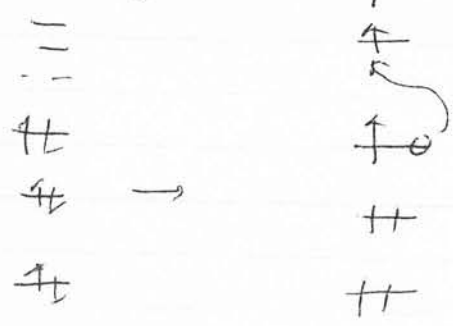
remove canonical orbital from HF.

Similar picture for electron-attachment.
(add electron in virtual orbital)

Singly excited states:

$$|\Psi_\lambda\rangle = \sum_{r,a} \hat{r}^+ \hat{a} \, |HF\rangle \, C_r^a$$

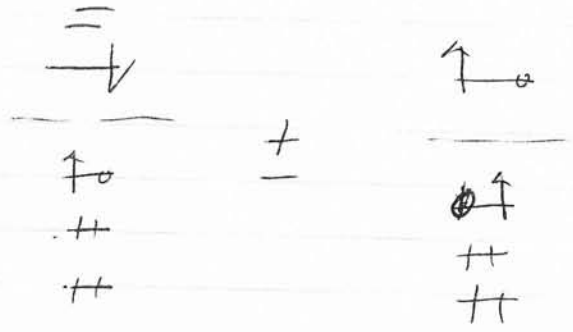
→ promote electron in orbital a (occupied in HF) to orbital r (unoccupied or virtual)



$\bar{a} \to r$ (remove β, populate α)

$r^+ \bar{a} \, |HF\rangle \to (\alpha\alpha)$ triplet state

$\bar{r}^+ a \, |HF\rangle \to (\beta\beta)$ triplet state



$r_\alpha^+ a_\alpha \, |HF\rangle + \bar{r}^+ \bar{a} \, |HF\rangle \to$ ~~triplet~~ Singlet

$r_\alpha^+ a_\alpha \, |HF\rangle - \bar{r}^+ \bar{a} \, |HF\rangle \to$ triplet

(always linear combination)

while for ionized and attached states we can define optimal "canonical" orbitals, such that states are single configurational (to good approximation) this is often not possible for excited states. We intrinsically need linear combination

$$\Psi_\lambda = \sum_{r,a} r^+ a \,|HF\rangle\, C_{ra}$$

(here r, a general spin-orbitals)

Let us consider matrix-elements

$$\sum h_{ij} \Big[\langle HF| b^+ s^+ i^+ j^+ r^+ a \,|HF\rangle : h_{sr}\,\delta_{ab}$$

$$+ \langle HF| b^+ s^+ i^+ j^+ r^+ a \,|HF\rangle : - \delta_{sr}\, h_{ab}$$

$$+ \langle HF| b^+ s^+ i^+ j^+ r^+ a \,|HF\rangle : + \delta_{ab}\,\delta_{sr} \sum_c h_{cc}$$

$$+\tfrac{1}{4} \langle ij||kl\rangle \Big[\langle HF| b^+ s^+ i^+ j^+ l k r^+ a \,|HF\rangle - \langle sa||rb\rangle$$

(*4)

$$+ \langle HF| b^+ s^+ i^+ j^+ l k r^+ a \,|HF\rangle \quad \delta_{ab} \sum_c \langle sc||rc\rangle$$

$$+ \langle HF| b^+ s^+ i^+ j^+ l k r^+ a \,|HF\rangle - \delta_{rs} \sum \langle ac||bc\rangle$$

$$+ \langle HF| b^+ s^+ i^+ j^+ l k r^+ a \,|HF\rangle + \delta_{sr}\,\delta_{ab}\, \langle HF|\hat{V}|HF\rangle$$

$$= \delta_{ab}\, f_{rs} - f_{ab}\,\delta_{rs} - \langle sa||rb\rangle + \delta_{sr}\,\delta_{ab}\, E_{HF}$$

Hilbert

It is seen that we can identify the fock matrix elements f_{rs} and f_{ab}

$\Rightarrow$ If we neglect $\langle sa||rb\rangle$ excitation energies $E_\lambda - E_{HF}$ are represented by difference in HF orbital energies. $(\varepsilon_r - \varepsilon_a)$

This is a very poor approximation however. The 2-electron term is vital.

We can meaningfully look at a single pair of excitations

	$r^+\bar{a}\,\lvert HF\rangle$	$\bar{r}^+\bar{a}\,\lvert HF\rangle$
$r^+\bar{a}\,\lvert HF\rangle$	$\varepsilon_r - \varepsilon_a \mp \langle ra\|\|ra\rangle$	$\langle r\bar{a}\,\lvert\, a\bar{r}\rangle$
$\bar{r}^+\bar{a}\,\lvert HF\rangle$	$\langle r\bar{a}\,\lvert\, a\bar{r}\rangle$	$\varepsilon_r - \varepsilon_a - \langle \bar{r}\bar{a}\|\|\bar{r}\bar{a}\rangle$

$\rightarrow \Xi = \varepsilon_r - \varepsilon_a - \underbrace{J_{ra}}_{\langle ra||ra\rangle} \pm K_{ra}$

$(-)$: triplet state

$(+)$: singlet state.

Can we understand ⊖ Sign in $\langle r\bar{a}|r\bar{a}\rangle$?

$$\varepsilon_r = h_{rr} + \sum_c \langle rc \| rc \rangle$$

$$\varepsilon_a = h_{aa} + \sum_c \langle ac \| ac \rangle$$

ε_r includes ~~all~~ V-interactions with all occupied orbitals.
However one interaction $\langle \bar{r}\bar{a} \| \bar{r}\bar{a} \rangle$ is missing → subtract from diagonal
(hence this is correcting the use of f-matrix-elements)

In ε_a we subtract all interactions that are missing compared to (HF)

Using the f-matrix-elements we obtain quite compact expressions for matrix elements.