CB2070 Ex. 4

① With the fock operator

$$\hat{f} = \hat{h} + \sum_i^N (\hat{J}_i - \hat{K}_i)$$

and

$$\hat{J}_i |\psi_a\rangle = \left[\int \frac{|\psi_i(\bar{r}')|^2}{|\bar{r} - \bar{r}'|} d\bar{r}'\right] |\psi_a\rangle$$

$$\hat{K}_i |\psi_a\rangle = \left[\int \frac{\psi_i^+(\bar{r}')\psi_a(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r}'\right] |\psi_i\rangle$$

For a Hermitian operator:

$$\hat{f} = \hat{f}^+ \quad , \quad f_{ab} = f_{ba}^*$$

Show $\langle a|\hat{f}|b\rangle = \langle a|\hat{f}^+|b\rangle = \langle b|\hat{f}|a\rangle^*$

Note $\langle a|\hat{f}^+|b\rangle = \langle b|\hat{f}|a\rangle^*$ for any operator matrix elements

$\hat{h}$

$$h_{ab} = \langle a|\hat{h}|b\rangle = \int \psi_a^+ \hat{h} \psi_b \, d\bar{r} = \left[\int \psi_a^+ \hat{h}^+ \psi_b \, d\bar{r}\right]^*$$

$\hat{h}$ is real (and we are assuming that the kinetic + potential operators are both Hermitian)★

$$= \left[\int \psi_b^+ \hat{h} \psi_a \, d\bar{r}\right]^* = \langle b|\hat{h}|a\rangle^* = h_{ba}^*$$

$\hat{J}$

$$(\hat{J})_{ab} = \langle a|\hat{J}_i|b\rangle = \iint \psi_a(\bar{r}) \frac{\psi_i^+(\bar{r}')\psi_i(\bar{r}')}{|\bar{r} - \bar{r}'|} \psi_b(\bar{r}) \, d\bar{r}' d\bar{r}$$

we use that $\langle a|\hat{J}_i|b\rangle = \langle b|\hat{J}_i^+|a\rangle^*$ (see lecture notes 2)

$$= \left[\iint \psi_b^+(\bar{r}) \left(\frac{\psi_i^+(\bar{r}')\psi_i(\bar{r}')}{|\bar{r} - \bar{r}'|}\right)^+ \psi_a(\bar{r}) \, d\bar{r}' d\bar{r}\right]^*$$

since $(\psi_i^+\psi_i)^+ = \psi_i\psi_i^+ = \psi_i^+\psi_i$ the operator fraction is unchanged

$$= \left[\iint \psi_b^+(\bar{r}) \frac{\psi_i^+(\bar{r}')\psi_i(\bar{r}')}{|\bar{r} - \bar{r}'|} \psi_a(\bar{r}) \, d\bar{r}' d\bar{r}\right]^* = \langle b|\hat{J}_i|a\rangle^* = (J_i)_{ba}^*$$

★ You can show it using integration by parts

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$\hat{K}$: $(\hat{K})_{ab} = \langle a|\hat{K}_i|b\rangle = \iint \psi_a^+(\bar{r}) \frac{\psi_i^+(\bar{r}')\psi_b(\bar{r}')}{|\bar{r}-\bar{r}'|}\psi_i(\bar{r})\,d\bar{r}'d\bar{r}$

again we use $\langle a|\hat{K}_i|b\rangle = \langle b|\hat{K}_i^+|a\rangle^*$

$$= \left(\iint \psi_i^+(\bar{r}) \frac{\psi_b^+(\bar{r}')\psi_i(\bar{r}')}{|\bar{r}-\bar{r}'|}\psi_a(\bar{r})\,d\bar{r}'d\bar{r}\right.$$

Here we let the operator work to the left

since we integrate over all space, we can exchange the $\bar{r}$ and $\bar{r}'$ variables and get

$$(\hat{K})_{ab} = \left(\iint \psi_b^+(\bar{r}) \frac{\psi_i^+(\bar{r}')\psi_a(\bar{r}')}{|\bar{r}'-\bar{r}|}\psi_i(\bar{r})\,d\bar{r}'d\bar{r}\right)^*$$

$$= \langle b|\hat{K}_i|a\rangle^* = (\hat{K})_{ba}^* \quad \Rightarrow \text{Hermitian}$$

Since $\hat{h}$, $\hat{J}$, and $\hat{K}$ have been shown to be Hermitian, then $\hat{f}$ is also Hermitian

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② $$E^{HF} = \sum_i^N \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{ij}^N [\langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle]$$

We introduce the Lagrangian

$$\mathcal{L} = E - \sum_{ij}^N \varepsilon_{ji}(\langle i|j\rangle - \delta_{ij})$$

$$= \sum_i^N \langle i|\hat{h}|i\rangle + \frac{1}{2}\sum_{ij}^N [\langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle]$$

$$- \sum_{ij}^N \varepsilon_{ij}(\langle i|j\rangle - \delta_{ij})$$

This one is a constant in the variation and cancels out

From the lecture notes:

$$\delta E[\Psi] = \langle \delta\Psi|\hat{H}|\Psi\rangle + \langle \Psi|\hat{H}|\delta\Psi\rangle$$

For set of two orbitals: $\langle \delta\psi_i \psi_j|\ldots|\psi_i\psi_j\rangle = \langle \psi_i \delta\psi_j|\ldots|\psi_i\psi_j\rangle$

We write

$\times 2 \cdot \frac{1}{2}$

$$\delta\mathcal{L} = \sum_i^N \langle \delta\psi_i|\hat{h}|\psi_i\rangle + \sum_{ij}^N [\underbrace{\langle \delta\psi_i\psi_j|\hat{g}|\psi_i\psi_j\rangle}_{\hat{J}_j} - \underbrace{\langle \delta\psi_i\psi_j|\hat{g}|\psi_j\psi_i\rangle}_{\hat{K}_j}]$$

$$- \sum_{ij}^N \varepsilon_{ji}\langle \delta\psi_i|\psi_j\rangle$$

complex conjugate

$$+ \sum_i^N \langle \psi_i|\hat{h}|\delta\psi_i\rangle + \sum_{ij}^N [\langle \psi_i\psi_j|\hat{g}|\delta\psi_i\psi_j\rangle - \langle \psi_i\psi_j|\hat{g}|\delta\psi_j\psi_i\rangle]$$

$$- \sum_{ij}^N \varepsilon_{ij}\langle \psi_i|\delta\psi_j\rangle = 0$$

$\varepsilon_{ji}^* = \varepsilon_{ij}$

our condition for the Lagrangian

We can separate the bra-state $\langle\delta\psi_i|$ from the rest
The first two sums we see can be condensed to the Fock operator operating on a ket-state $|\psi_i\rangle$

$$= \sum_i^N \langle \delta\psi_i| \Big[\Big(\hat{h} + \sum_j \hat{J}_j - \hat{K}_j\Big)|\psi_i\rangle - \sum_j \varepsilon_{ji}|\psi_j\rangle = 0$$

For the above to be zero for an arbitrary variation $\langle\delta\psi_i|$, the following must be true

$$\Rightarrow \hat{f}|\psi_i\rangle - \sum_j \varepsilon_{ji}|\psi_j\rangle = 0$$