CB2070 Ex. 5

1.a Introduce unitary transformation

$$|\psi_i'\rangle = \sum_{j=1}^{N} |\psi_j\rangle \bar{U}_{ji} \quad , \quad \langle \psi_i'| = \sum_{j}^{N} \langle \psi_j | U_{ji}^*$$

$$U^\dagger U = \mathbb{1} \rightarrow (U^\dagger U)_{ij} = \delta_{ij}$$

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

$$\hat{J}_j |\psi_i\rangle = \int \frac{|\psi_j(\bar{r}')|^2}{|\bar{r} - \bar{r}'|} d\bar{r}' |\psi_i\rangle$$

$$\hat{K}_j |\psi_i\rangle = \int \frac{\psi_j^*(\bar{r}')\psi_i(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r}' |\psi_j\rangle$$

$\hat{h}$ does not depend on the orbitals $\Rightarrow$ invariant

$$\sum_i \langle \psi_i' | \hat{h} | \psi_i' \rangle = \sum_{k,l} \sum_i U_{ki}^* U_{li} \langle \psi_k | \hat{h} | \psi_l \rangle = \sum_{k,l} \delta_{kl} \langle \psi_k | \hat{h} | \psi_l \rangle$$

$$= \sum_i \langle \psi_i | \hat{h} | \psi_i \rangle$$

$\hat{J}_i$ in new basis

$$\hat{J}' = \sum_j \hat{J}_j' = \sum_j \int \frac{\psi_j^{*\prime}(\bar{r}')\psi_j'(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r}'$$

$$= \underbrace{\sum_j \sum_{k,l} U_{kj}^* U_{lj}}_{\sum_j U_{kj}^* U_{lj} = (U^\dagger U)_{kl} = \delta_{kl}} \int \frac{\psi_k^*(\bar{r}')\psi_l(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r}' = \sum_{k,l} \delta_{kl} \int \frac{\psi_k(\bar{r}')\psi_l(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r}'$$

$$= \sum_i \int \frac{|\psi_i(\bar{r}')|^2}{|\bar{r} - \bar{r}'|} d\bar{r}' = \hat{J}$$

$$\hat{K}' = \sum_j \hat{K}_j' = \int \frac{\psi_j'(\bar{r}')\psi_i'(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r}' = \sum_{k,l} \sum_j U_{kj}^* U_{li} \frac{\psi_k(\bar{r}')\psi_l(\bar{r}')}{|\bar{r} - \bar{r}'|} d\bar{r}'$$

Include a ket $|\psi_j'(\bar{r})\rangle$

$$\sum_{k,l,m} \sum_j U_{kj}^* U_{li} U_{mj} \int \frac{\psi_k^*(\bar{r}')\psi_l(\bar{r}')}{|\bar{r} - \bar{r}'|} \psi_m(\bar{r}) d\bar{r}' =$$

$$= \sum_{k,l,m} \delta_{km} \int \frac{\psi_k^* \psi_l}{|\bar{r} - \bar{r}'|} \psi_m d\bar{r}' = \sum_{k,l} U_{li} \int \frac{\psi_k^* \psi_l}{|\bar{r} - \bar{r}'|} \psi_k d\bar{r}' =$$

Replace $\sum_l U_{li} \psi_l$ with an orbital in the transformed basis. ψ_i'

$$= \sum_k \int \frac{\psi_k^*(\bar{r}')\psi_i'(\bar{r}')}{|\bar{r}-\bar{r}'|} d\bar{r}' \psi_k(\bar{r}) = \sum_j \hat{K}_j |\psi_i'\rangle$$

where dummy index k is replaced by j.
It has now been shown that

$$\hat{K}' |\psi_i'\rangle = \hat{K} |\psi_i'\rangle$$

(1.6) Choose U such that

$$F_{ij}' = \langle \psi_i' | \hat{f} | \psi_j' \rangle = \sum_{k,l} U_{ki}^* U_{lj} \langle \psi_k | \hat{f} | \psi_l \rangle = F_{ii}' \delta_{ij}$$

We have the HF equations

$$\hat{f} |\psi_a\rangle = \sum_b \varepsilon_{ba} |\psi_b\rangle$$

Only diagonal elements are nonzero:

$$F_{ij}' = \langle \psi_i' | \hat{f} | \psi_j' \rangle = \sum_{k,l} U_{ki}^* U_{lj} \langle \psi_k | \hat{f} | \psi_l \rangle = \sum_{k,l} U_{ki}^+ U_{lj} \underbrace{\langle \psi_k | \sum_m \varepsilon_{ml} | \psi_m \rangle}_{\sum_m \varepsilon_{ml} \langle k | m \rangle = \varepsilon_{kl}}$$

$$= \sum_{k,l} U_{ki}^* U_{lj} \varepsilon_{kl} = \sum_{k,l} U_{ki}^* \varepsilon_{kl} U_{lj}$$

U has been chosen such that it diagonalizes $\hat{f}$ and, thus, ε

$$F_{ij}' = F_{ii}' \delta_{ij} = \varepsilon_i \delta_{ij}$$

Thus, the only nonzero elements are

$$\langle \psi_a | \hat{f} | \psi_a \rangle = \varepsilon_a \quad , \quad \hat{f} |\psi_a\rangle = \varepsilon_a |\psi_a\rangle$$

where the prime has been left out on the transformed spinorbitals

ALTERNATIVELY

$$F_{ij}' = F_{ii}' \delta_{ij} = \langle i' | \hat{f} | i \rangle \delta_{ij} = \langle i' | \sum_k \varepsilon_{ik} | k \rangle \delta_{ij} = \delta_{ij} \sum_k \varepsilon_{ik} \langle i' | k \rangle$$

$$= \varepsilon_i \delta_{ij} \Rightarrow F_{ii}' = \varepsilon_i$$

We can write $\langle i | (\hat{f} | i \rangle - \varepsilon_i | i \rangle) = 0 \Rightarrow \hat{f} |\psi_i'\rangle = \varepsilon_i |\psi_i'\rangle$

CB2070 Ex 5 cont'd

② Show that

$$IP = E_i^{N-1} - E_{HF}^{N} = -\varepsilon_i$$

$$EA = E_{HF}^{N} - E_s^{N+1} = -\varepsilon_s$$

$$E_{HF}^{N} = \sum_{j}^{N} \langle j|\hat{h}|j\rangle + \frac{1}{2}\sum_{j,k}^{N}\left(\langle j|\hat{J}_k|j\rangle - \langle j|\hat{K}_k|j\rangle\right)$$

$$E_i^{N-1} = \sum_{j\neq i}^{N-1} \langle j|\hat{h}|j\rangle + \frac{1}{2}\sum_{j,k\neq i}^{N-1} \langle j|\hat{J}_k|j\rangle - \langle j|\hat{K}_k|j\rangle$$

For IP, first look at one-elec parts

$$E_i^{N-1}(\text{1-elec}) - E_{HF}^{N}(\text{1-elec}) = \sum_{j\neq i}^{N-1}\langle j|\hat{h}|j\rangle - \Bigg[\underbrace{\langle i|\hat{h}|i\rangle + \sum_{j\neq i}^{N-1}\langle j|\hat{h}|j\rangle}_{E^N}\Bigg] = -\langle i|\hat{h}|i\rangle$$

We decompose the two-electron part of the full energy

$$E_{HF}^{N}(\text{2-elec}) = \frac{1}{2}\sum_{j}^{N}\sum_{k}^{N}\langle jk|\hat{g}|jk\rangle - \langle jk|\hat{g}|kj\rangle$$

$$= \frac{1}{2}\sum_{k\neq i}^{N-1}\left[\langle ik|\hat{g}|ki\rangle - \langle ik|\hat{g}|ki\rangle\right] + \frac{1}{2}\sum_{j\neq i}\left[\langle ji|\hat{g}|ji\rangle - \langle ji|\hat{g}|ij\rangle\right]$$

$$+ \frac{1}{2}\sum_{j\neq i}^{N-1}\sum_{k\neq i}^{N-1}\left[\langle jk|\hat{g}|jk\rangle - \langle jk|\hat{g}|kj\rangle\right]$$

The two-elec part for the ionized system is

$$E_i^{N-1}(\text{2-elec}) = \sum_{j\neq i}^{N-1}\sum_{k\neq i}^{N-1}\left[\langle jk|\hat{g}|jk\rangle - \langle jk|\hat{g}|kj\rangle\right]$$

We recognize this double-sum for the decomposition of the ground state energy. Thus:

$$E_i^{N-1}(\text{2-elec}) - E_{HF}^{N}(\text{2-elec}) = -\frac{1}{2}\sum_{k\neq i}^{N-1}\left[\langle ik|\hat{g}|ik\rangle - \langle ik|\hat{g}|ki\rangle\right]$$

$$-\frac{1}{2}\sum_{j\neq i}^{N-1}\left[\langle ji|\hat{g}|ji\rangle - \langle ji|\hat{g}|ij\rangle\right]$$

If j or k = i, both sums will yield a zero-term. We can then remove the restriction and see that the two sums become identical due to the indistinguishable particles

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② cont'd The IP two-electron part then becomes

$$E^{IP}(2\text{-elec}) = -\sum_{j}^{N}\left[\langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle\right]$$

Putting the one- and two-electron terms together, we get

$$E^{IP} = -\langle i|\hat{h}|i\rangle - \sum_{j}^{N}\left[\langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle\right] = -\varepsilon_i$$

which is the orbital energy of the HOMO

Continue to the electron affinity

$$E^{EA} = E_{HF}^{N} - E_{s}^{N+1}$$

With a similar approach, we get

$$E^{EA}(1\text{-elec}) = \sum_{i}^{N}\langle i|\hat{h}|i\rangle - \sum_{i}^{N+1}\langle i|\hat{h}|i\rangle$$

$$= \sum_{i}^{N}\langle i|\hat{h}|i\rangle - \sum_{i\neq s}^{N}\langle i|\hat{h}|i\rangle - \langle s|\hat{h}|s\rangle$$

$$= -\langle s|\hat{h}|s\rangle$$

$$E^{EA}(2\text{-elec}) = \frac{1}{2}\sum_{i,j}^{N}\langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle - \frac{1}{2}\sum_{i,j}^{N+1}\langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle$$

$$= \frac{1}{2}\sum_{i,j}^{N}\langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle - \frac{1}{2}\sum_{j\neq s}^{N}\langle sj|\hat{g}|sj\rangle - \langle sj|\hat{g}|js\rangle$$

$$-\frac{1}{2}\sum_{i\neq s}^{N}\langle is|\hat{g}|is\rangle - \langle is|\hat{g}|si\rangle - \frac{1}{2}\sum_{i,j\neq s}\langle ij|\hat{g}|ij\rangle - \langle ij|\hat{g}|ji\rangle$$

$$= -\frac{1}{2}\sum_{j\neq s}^{N}\langle sj|\hat{g}|sj\rangle - \langle sj|\hat{g}|js\rangle - \frac{1}{2}\sum_{i\neq s}^{N}\langle is|\hat{g}|is\rangle - \langle is|\hat{g}|si\rangle$$

As before, we can remove the restriction in the two sums, and they will be identical. Thus:

$$E^{EA} = -\langle s|\hat{h}|s\rangle - \sum_{j}^{N}\langle sj|\hat{g}|sj\rangle - \langle sj|\hat{g}|js\rangle = -\varepsilon_s$$

which is the orbital energy of the LUMO