Relationship between the Hartree-Fock eigenvalues and the total electronic energy

Let's first consider the unrestricted case. If we label the spatial part of the α spin orbitals as ϕ_i and the spatial part of the β spin orbitals as γ_i we may write the electronic energy as

$$E = \sum_{i=1}^{N_\alpha} \langle \phi_i | \hat{f} + \frac{1}{2}\left(\hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\alpha\right) | \phi_i \rangle + \sum_{i=1}^{N_\beta} \langle \gamma_i | \hat{f} + \frac{1}{2}\left(\hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\beta\right) | \gamma_i \rangle$$

recognizing that $\hat{F}^\alpha = \hat{f} + \hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\alpha$ and $\hat{F}^\beta = \hat{f} + \hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\beta$

we have

$$E = \frac{1}{2}\sum_{i=1}^{N_\alpha} \langle \phi_i | \hat{f} + \hat{F}^\alpha | \phi_i \rangle + \frac{1}{2}\sum_{i=1}^{N_\beta} \langle \gamma_i | \hat{f} + \hat{F}^\beta | \gamma_i \rangle$$

or

$$E = \frac{1}{2}\sum_{i=1}^{N_\alpha} \left(\langle \phi_i | \hat{f} | \phi_i \rangle + \varepsilon_i^\alpha \right) + \frac{1}{2}\sum_{i=1}^{N_\beta} \left(\langle \gamma_i | \hat{f} | \gamma_i \rangle + \varepsilon_i^\beta \right)$$

One can write this in another form by noting

$$\hat{f} + \frac{1}{2}\left(\hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\alpha\right) = \hat{F}^\alpha - \frac{1}{2}\left(\hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\alpha\right)$$

and

$$\hat{f} + \frac{1}{2}\left(\hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\beta\right) = \hat{F}^\beta - \frac{1}{2}\left(\hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\beta\right)$$

And so

$$E = \sum_{i=1}^{N_\alpha} \left(\varepsilon_i^\alpha - \frac{1}{2} \langle \phi_i | \hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\alpha | \phi_i \rangle \right) + \sum_{i=1}^{N_\beta} \left(\varepsilon_i^\beta - \frac{1}{2} \langle \gamma_i | \hat{J}^\alpha + \hat{J}^\beta - \hat{K}^\beta | \gamma_i \rangle \right)$$

We see that the sum of the Hartree-Fock eigenvalues in not equal to the total electronic energy.
If we consider the closed shell case we have $N_\alpha = N_\beta = N/2$ and $\phi_i = \gamma_i$ so that

$$E = \sum_{i=1}^{N/2} \left(\langle \phi_i | \hat{f} | \phi_i \rangle + \varepsilon_i \right)$$

or

$$E = \sum_{i=1}^{N/2} \left(2\varepsilon_i - \langle \phi_i | 2\hat{J} - \hat{K} | \phi_i \rangle \right)$$