Hartree-Fock total energy and sum of orbital energies

Shorthand notation

$$\varphi_\alpha(\mathbf{r}) \quad \rightarrow \quad |\varphi_\alpha\rangle \quad \rightarrow \quad |\alpha\rangle$$

Slater determinant

$$\Phi_{\alpha,\beta,....,\nu} \quad \rightarrow \quad |\alpha, \beta, ..., \nu\rangle$$

We have started our work with the Hartree-Fock equations by evaluating

$$\langle\Phi_{\alpha,\beta,....,\nu}| \left[T + V + \sum_{pairs\ ij} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}\right] |\Phi_{\alpha,\beta,....,\nu}\rangle \tag{1}$$

This we have evaluated as

$$\langle\Phi|\ H\ |\Phi\rangle \quad = \quad \sum_\alpha \langle\alpha|(T+V)|\alpha\rangle + \sum_{pairs\ \alpha\beta} [\langle\alpha\beta|V_{ee}|\alpha\beta\rangle - \langle\alpha\beta|V_{ee}|\beta\alpha\rangle] \tag{2}$$

From this expression we have obtained Hartree-Fock equations by the variational procedure.

The Hartree-Fock equation can be then written as

$$\left[T + V + \sum_{\beta} \langle\beta| \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\beta\rangle\right] |\alpha\rangle - \sum_{\beta} \left[\langle\beta| \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\alpha\rangle\right] |\beta\rangle \quad = \quad \varepsilon_\alpha |\alpha\rangle \qquad (3)$$

We form the matrix element with the given $\langle\alpha|$

$$\langle\alpha| \left[T + V + \sum_{\beta} \langle\beta| \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\beta\rangle\right] |\alpha\rangle - \langle\alpha| \left[\sum_{\beta} \langle\beta| \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} |\alpha\rangle\right] |\beta\rangle \quad = \quad \varepsilon_\alpha \qquad (4)$$

since $\langle\alpha|\alpha\rangle = 1$. This can be rewritten as

$$\varepsilon_\alpha \quad = \quad \langle\alpha|(T+V)|\alpha\rangle + \sum_{\beta\neq\alpha} [\langle\beta\alpha|V_{ee}|\beta\alpha\rangle - \langle\beta\alpha|V_{ee}|\alpha\beta\rangle] \qquad (5)$$

And now we can explore what is the sum of all ε_α

$$\sum_\alpha \varepsilon_\alpha \quad = \quad \sum_\alpha \langle\alpha|(T+V)|\alpha\rangle + \sum_\alpha \sum_{\beta\neq\alpha} [\langle\beta\alpha|V_{ee}|\beta\alpha\rangle - \langle\beta\alpha|V_{ee}|\alpha\beta\rangle] \qquad (6)$$

which we can compare with the above $\langle\Phi|\ H\ |\Phi\rangle$

$$\langle\Phi|\ H\ |\Phi\rangle \quad = \quad \sum_\alpha \langle\alpha|(T+V)|\alpha\rangle + \sum_{pairs\ \alpha\beta} [\langle\alpha\beta|V_{ee}|\alpha\beta\rangle - \langle\alpha\beta|V_{ee}|\beta\alpha\rangle] \qquad (7)$$

The two expressions are very similar, but they differ in fact by all the interaction term, since it is counted twice in the sum:

$$\sum_{\alpha} \sum_{\beta \neq \alpha} F_{\alpha\beta} \quad = \quad 2 \sum_{pairs\ \alpha\beta} F_{\alpha\beta}$$

for any set of objects that are symmetric $F_{\alpha\beta} \ = \ F_{\beta\alpha}$

Our objects are symmetric, because they are in fact of the type $H_{\alpha\beta,\alpha\beta}$. The wavefunctions are antisymmetric, $|\alpha\beta\rangle = -|\beta\alpha\rangle$.

Thus, surprisingly perhaps

$$\langle\Phi|\ H\ |\Phi\rangle \quad = \quad \sum_{\alpha} \varepsilon_{\alpha} - \sum_{pairs\ \alpha\beta} [\langle\alpha\beta|V_{ee}|\alpha\beta\rangle - \langle\alpha\beta|V_{ee}|\beta\alpha\rangle] \qquad (8)$$