Hartrre-Fock orbital energies

Eigenvalues of Fock Operator

Physically the orbital energy represents the energy required to remove an electron from that orbital when all other orbitals remain the same as in the neutral system. This is Koopmanns theorem

For Lithium we have the following

Process	energy (ev)	orbital energy (ev)
Li ($1s^2 2s^1$; ^1S) ----- Li$^+$ ($1s^2$; ^2S)	5.390	5.342
Li ($1s^2 2s^1$; ^1S) -- Li$^+$ ($1s^1 2s^1$;$^{1\text{ or }3}$ S)	??????	67.42

A consequence of this property is that the sum of the orbital (one-electron) energies of an atom is NOT the total energy of the atom

Consider

$2\ \varepsilon_{1s} + \varepsilon_{2s}$ = -5.1517 au

E(Hartree-Fock) = - -7.433 au

$$E_{HF} = \int \psi^* \hat{H} \psi dV$$

$$E_{HF} = \sum_{i=1}^{3} \varepsilon_i - \sum_{i=1}^{3} \int \varphi_i^* V_{HF} \varphi dV$$

$$V_{HF} = \sum_{i=1}^{3} \int d\tau(2) \varphi_i^*(2) \frac{1}{r_{12}} (1 - \hat{P}_{12}) \varphi_i(2)$$