Correlation Energy

Consider the wavefunction for He

$$\Psi(1,2) = \Psi(x_1, y_1, z_1, x_2, y_2, z_2)$$

$$P(1,2) = \Psi(1,2)^* \Psi(1,2)$$

represents the probability/volume of finding a particle at point point 1 while the other is at point 2. Clearly we can not find both particles at the same point in space because the Coulomb energy would be infinite. This means that for the exact wavefunction

$$P(1,1) = 0$$

Consider the Hartree-Fock wavefunction for He

$$\Psi_{HF}(1,2) = \varphi(1)\varphi(2)$$

and the associated probability distribution

$$P_{HF}(1,2) = \varphi^2(1)\varphi^2(2)$$

Clearly

$$P_{HF}(1,1) = \varphi^2(1)\varphi^2(1) = \varphi^4(1) \neq 0$$

which is a failing of the Hartree-Fock method. This error in the Hartree-Fock method is called the correlation error.

The Hartree-Fock energy for He is -2.8617 au while the exact non-relativsitic energy is -2.9037 au and the difference 0.0420 au or 1.14 eV is the correlation energy for He. While small relative to the total energy the correlation error is chemically significant.