

10.9: Correlation Energy and Configuration Interaction

The Hartree-Fock energy is not as low as the exact energy. The difference is due to electron correlation effects and is called the **correlation energy**. The Hartree-Fock wavefunction does not include these correlation effects because it describes the electrons as moving in the average potential field of all the other electrons. The instantaneous influence of electrons that come close together at some point is not taken into account. Electrons repel each other, and they will try to stay away from each other. Their motion therefore is correlated, and this correlation reduces the energy of the system because it reduces the electron-electron repulsion. The Hartree-Fock wavefunction does not account for this correlation and therefore produces an energy that is too high.

One method for accounting for these correlation effects and the correlation energy is called **configuration interaction (CI)**. In configuration interaction, Slater determinants are formed from two or more orbital occupation configurations. The CI wavefunction then is written as a linear combination of these determinants, and the coefficients are determined to minimize the energy.

$$\psi_{CI} = c_1 D_1 + c_2 D_2 \quad (10.9.1)$$

Good quality one-electron molecular orbitals are obtained by using a large basis set, by optimizing the parameters in the functions with the variational method, and by accounting for the electron-electron repulsion using the self-consistent field method. Electron correlation effects are taken into account with configuration interaction. The CI methodology means that a wavefunction is written as a series of Slater Determinants involving different configurations, just as we discussed for the case of atoms. The limitation in this approach is that computer speed and capacity limit the size of the basis set and the number of configurations that can be used.

Exercise 10.9.1

Define correlation energy and explain why it is omitted in a SCF calculation and how it is included in a CI calculation.

Exercise 10.9.2

Write a CI wavefunction for helium using Slater determinants for the $1s^2$ and $1s1s^1$ configurations. Explain how addition of the $1s^1 2s^1$ configuration to the wavefunction accounts for electron correlation in terms of keeping the electrons apart in different regions of space

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