

9.8: Configuration Interaction

The best energies obtained at the Hartree-Fock level are still not accurate, because they use an average potential for the electron-electron interactions. Configuration interaction (CI) methods help to overcome this limitation. Because electrons interact and repel each other, their motion in atoms is correlated. When one electron is close to the nucleus, the other tends to be far away. When one is on one side, the other tends to be on the other side. This motion is related to that of two people playing tag around a house. As we said before, the exact wavefunction must depend upon the coordinates of both electrons simultaneously. We have shown that it is a reasonable approximation in calculating energies to neglect this correlation and use wavefunctions that only depend upon the coordinates of one electron, which assumes the electrons move independently. This "orbital approximation" is similar to playing tag without keeping track of the other person. This independent-electron approximation gives reasonable, even good values, for the energy, and correlation can be taken into account to improve this description even more. The method for taking correlation into account is called **Configuration Interaction**.

In describing electrons in atoms, it is not necessary to be restricted to only a single orbital configuration given by a [Slater determinant](#). We developed the Slater determinant as a way to create correctly antisymmetrized product wavefunctions that approximate the exact multi-electron function for an atom. By using more than one configuration and putting electrons in different orbitals, spatial correlations in the electron motion can be taken into account. This procedure is called Configuration Interaction (CI).

For example, for the two-electron Slater determinant wavefunction of helium, we could write

$$\psi(r_1, r_2) = \underbrace{c_1 \text{Det}[\varphi_{1s}(r_1)\varphi_{1s}(r_2)]}_{\text{ground state: } 1s^2} + \underbrace{c_2 \text{Det}[\varphi_{1s}(r_1)\varphi_{2s}(r_2)]}_{\text{excited state: } 1s^1 2s^1} \quad (9.8.1)$$

where c_1 and c_2 are coefficients (that can be varied in variational method). This wavefunction adds the excited (higher energy) configuration $1s^1 2s^1$ to the ground (lowest energy) configuration $1s^2$. The lowest energy configuration corresponds to both electrons being in the same region of space at the same time; the higher energy configuration represents one electron being close to the nucleus and the other electron being further away. This makes sense because the electrons repel each other. When one electron is in one region of space, the other electron will be in another region. Configuration interaction is a way to account for this correlation.

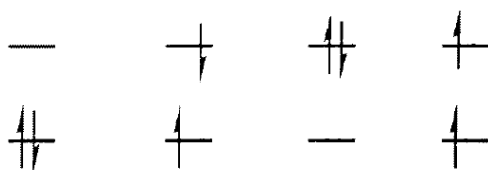


Figure 9.8.1: Within the CI approach the wavefunction for helium is a combination of all possible configurations (themselves described by Slater determinants). The wavefunction in Equation 9.8.1 would be the two left configurations

Exercise 9.8.1

Write a paragraph without using any equations that describes the essential features of configuration interaction.

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