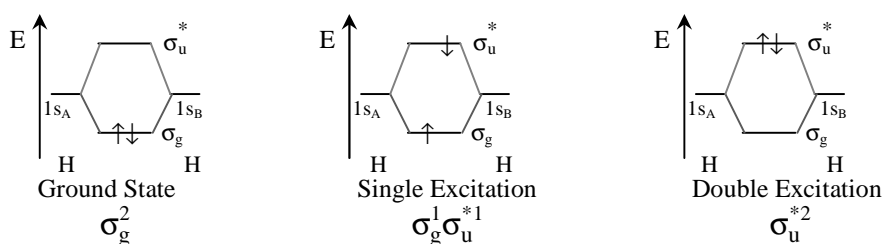


Electron Correlation - Configuration Interaction

Because electrons are negatively charged, electrons like to avoid each other. When one electron moves, the positions of the other electrons in the molecule adjust to minimize electron-electron repulsion. Therefore, the motions of the electrons are not independent; the motion of the electrons is correlated. The current best method for adjusting the molecular wave functions for electron correlation is called configuration interaction, CI. CI calculations allow the ground state of a molecule to mix with excited states of the molecule. For example for the H_2 molecule, the ground state configuration and several excited states are diagrammed below.



In CI calculations the ground state wave function is allowed to be a combination of all of the possible excited states:

$$E_{gs} = 0.9987^* \left[\begin{array}{c} E \\ \uparrow \\ \text{Diagram 1: } \sigma_g^2 \end{array} \right] + 0.0518^* \left[\begin{array}{c} E \\ \uparrow \\ \text{Diagram 2: } \sigma_g^1 \sigma_u^{*1} \end{array} \right] \quad 1$$

The coefficients in the linear combinations are calculated to minimize the energy of the ground state. (The calculation above is for at AM1) The advantage of mixing in excited state character to the ground state is that excited states have nodes between the nuclei, which help the electrons avoid each other.

The mixing of the ground state wave functions and the excited state wave functions can be done variationally. The coefficients for each excited configuration are adjusted to give the minimum ground state energy. This approach leads to techniques called CISD or CISDT. CISD includes single and double excitations. CISDT includes single, double, and triple excitations. The single excitation contributes most in CISD calculations. An easier approach is to use perturbation theory. The MP2 method uses second order perturbation theory to calculate the mixing of the various states. Remember that to calculate the correction to the wave function caused by a perturbation is given as:

$$\Psi_i \cong \Psi_i^{(0)} + \lambda \sum_{k \neq i} \frac{\mathcal{H}'_{ki}}{E_i^{(0)} - E_k^{(0)}} \Psi_k^{(0)} \quad \text{where } \mathcal{H}'_{ki} = \int \Psi_i^{(0)*} \mathcal{H}' \Psi_k^{(0)} d\tau$$

That is, the new wave function is a combination of all the other wave functions k , but the wave functions that are closest in energy to i are most important. In MP2 calculations, single excitations don't contribute; only double and higher excitations contribute. Eq. 1 is the MP2 result. Of course, for H_2 only single and double excitations are allowed since H_2 has only two electrons.