13.18: Frontier Orbitals

We said before that the energy of the electrons determine the behavior of the molecule. The populated energy levels contribute to the energy and behavior of the molecule. The other energy levels are only possibilities. The only case in which these orbitals are considered is when we think about adding additional electrons to the structure. That can happen during a reduction reaction, for instance. In that case, the next energy level may be a reasonable place to put another electron.

This description may be an approximation. Once another electron is added to the molecule, repulsive and attractive forces have been changed within the molecule, so the energies of all the electrons would have to adjust. Nevertheless, the LUMO is a good first guess at where an additional electron would go and what its energy would be.

Conversely, if a molecule is going to donate an electron (or an electron pair) in a reaction, frequently the electrons come from the highest occupied molecular orbital (HOMO). These electrons are often the most reactive, both because of their high energy and their accessible location, usually farther from the nucleus or on the edge of the molecule.

HOMO and LUMO orbitals are together called frontier orbitals, because they are at the edge of the real, occupied orbitals and the imaginary, unoccupied ones. Frontier orbitals are often considered when trying to understand reactions.

- The lowest unoccupied molecular orbital (LUMO) may describe an additional electron added to a molecule.
- An additional electron added to the molecule could have this energy and could be located in the area of space described by this orbital.