

14 The Importance of Symmetry

This chapter discusses the application of symmetry to orbital-based computational chemistry problems. A number of textbooks on symmetry are listed in the bibliography at the end of this chapter.

The symmetry of a molecule is defined by determining how the nuclei can be exchanged without changing its identity, conformation, or chirality. For example, a methane molecule can be turned about the axis connecting the carbon and one of the hydrogens by 120° and it is indistinguishable from the original orientation. Alternatively, symmetry can be considered a way of determining which regions of space around the molecule are completely equivalent. This second description is important because it indicates a means for calculations to be performed more quickly.

In order to obtain this savings in the computational cost, orbitals are symmetry-adapted. As various positive and negative combinations of orbitals are used, there are a number of ways to break down the total wave function. These various orbital functions will obey different sets of symmetry constraints, such as having positive or negative values across a mirror plane of the molecule. These various symmetry sets are called irreducible representations.

Molecular orbitals are not unique. The same exact wave function could be expressed an infinite number of ways with different, but equivalent orbitals. Two commonly used sets of orbitals are localized orbitals and symmetry-adapted orbitals (also called canonical orbitals). Localized orbitals are sometimes used because they look very much like a chemist's qualitative models of molecular bonds, lone-pair electrons, core electrons, and the like. Symmetry-adapted orbitals are more commonly used because they allow the calculation to be executed much more quickly for high-symmetry molecules. Localized orbitals can give the fastest calculations for very large molecules without symmetry due to many long-distance interactions becoming negligible.

Another reason that symmetry helps the calculations is that the Hamiltonian matrix will become a block diagonal matrix with one block for each irreducible representation. It is not necessary for the program to compute overlap integrals between orbitals of different irreducible representations since the overlap integrals will be zero by symmetry. Some computer programs go to the length of actually completing an SCF calculation as a number of small Hamiltonian matrices for each irreducible representation rather than one large Hamiltonian matrix. When this is done, the number of orbitals of each irreducible representation that are occupied must be defined at the beginning of the calculation

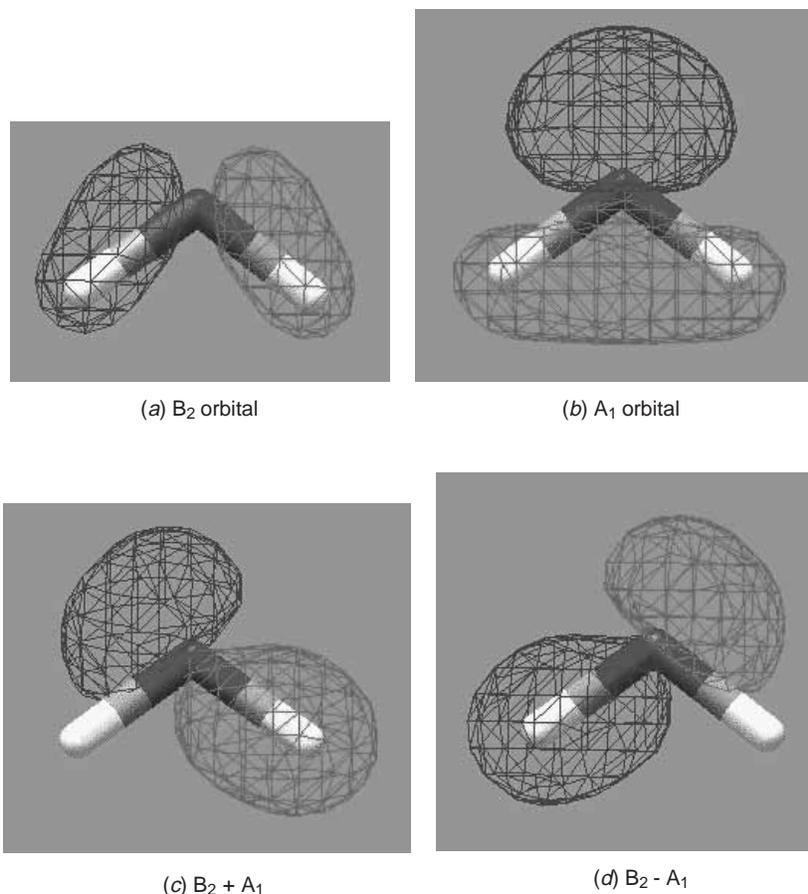


FIGURE 14.1 An illustration of symmetry-adapted vs. localized orbitals for water. (a, b) B_2 and A_1 symmetry-adapted orbitals. (c) Sum of these orbitals, which gives a localized orbital that is the bond between the oxygen and the hydrogen on the right. (d) Difference between these orbitals, which gives a localized orbital that is the bond between the oxygen and the hydrogen on the left.

either by the user or the program. Electrons will not be able to shift from one symmetry to another. Thus, the ground-state wave function cannot be determined unless the correct electron symmetry assignments were chosen originally. This can be an advantage since it is a way of obtaining excited-state wave functions, and fewer SCF convergence problems arise with this algorithm. The disadvantage is that the automated assignment algorithm may not find the correct ground state.

There is always a transformation between symmetry-adapted and localized orbitals that can be quite complex. A simple example would be for the bonding orbitals of the water molecule. As shown in Figure 14.1, localized orbitals can

be constructed from positive and negative combinations of symmetry-adapted orbitals. Some computer programs have localization algorithms that are more sophisticated than this.

14.1 WAVE FUNCTION SYMMETRY

In SCF problems, there are some cases where the wave function must have a lower symmetry than the molecule. This is due to the way that the wave function is constructed from orbitals and basis functions. For example, the carbon monoxide molecule might be computed with a wave function of C_{4v} symmetry even though the molecule has a $C_{\infty v}$ symmetry. This is because the orbitals obey C_{4v} constraints.

Most programs that employ symmetry-adapted orbitals only use Abelian symmetry groups. Abelian groups are point groups in which all the symmetry operators commute. Often, the program will first determine the molecule's symmetry and then use the largest Abelian subgroup. To our knowledge, the only software package that can utilize non-Abelian symmetry groups is Jaguar.

14.2 TRANSITION STRUCTURES

Transition structures can be defined by nuclear symmetry. For example, a symmetric S_N2 reaction will have a transition structure that has a higher symmetry than that of the reactants or products. Furthermore, the transition structure is the lowest-energy structure that obeys the constraints of higher symmetry. Thus, the transition structure can be calculated by forcing the molecule to have a particular symmetry and using a geometry optimization technique.

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