4.3: Sizes and Energies

The size (e.g., average value or expectation value of the distance from the atomic nucleus to the electron) of an atomic orbital is determined primarily by its principal quantum number n and by the strength of the potential attracting an electron in this orbital to the atomic center (which has some l-dependence too). The energy (with negative energies corresponding to bound states in which the electron is attached to the atom with positive binding energy and positive energies corresponding to unbound scattering states) is also determined by n and by the electrostatic potential produced by the nucleus and by the other electrons. Each atom has an infinite set of orbitals of each l quantum number ranging from those with low energy and small size to those with higher energy and larger size.

Atomic orbitals are solutions to an orbital-level Schrödinger equation in which an electron moves in a potential energy field provided by the nucleus and all the other electrons. Such one-electron Schrödinger equations are discussed, as they pertain to qualitative and semi-empirical models of electronic structure in Appendix F. The spherical symmetry of the one-electron potential appropriate to atoms and atomic ions is what makes sets of the atomic orbitals degenerate. Such degeneracies arise in molecules too, but the extent of degeneracy is lower because the molecule's nuclear coulomb and electrostatic potential energy has lower symmetry than in the atomic case. As will be seen, it is the symmetry of the potential experienced by an electron moving in the orbital that determines the kind and degree of orbital degeneracy which arises.

Symmetry operators leave the electronic Hamiltonian **H** invariant because the potential and kinetic energies are not changed if one applies such an operator R to the coordinates and momenta of **all** the electrons in the system. Because symmetry operations involve reflections through planes, rotations about axes, or inversions through points, the application of such an operation to a product such as **H**ψ gives the product of the operation applied to each term in the original product. Hence, one can write:

$$R(\mathbf{H}\psi) = (R\mathbf{H})(R\psi).$$

Now using the fact that **H** is invariant to R, which means that (R**H**) = **H**, this result reduces to:

$$R(\mathbf{H}\psi) = \mathbf{H}(R\psi),$$

which says that R commutes with **H**:

$$[R, \mathbf{H}] = 0$$

Because symmetry operators commute with the electronic Hamiltonian, the wavefunctions that are eigenstates of **H** can be labeled by the symmetry of the point group of the molecule (i.e., those operators that leave **H** invariant). It is for this reason that one constructs symmetry-adapted atomic basis orbitals to use in forming molecular orbitals.