5.4: Atoms

> *Atoms belong to the full rotation symmetry group; this makes their symmetry analysis the most complex to treat.*

In moving from linear molecules to atoms, additional symmetry elements arise. In particular, the potential field experienced by an electron in an orbital becomes invariant to rotations of arbitrary amounts about the x, y, and z axes; in the linear-molecule case, it is invariant only to rotations of the electron's position about the molecule's symmetry axis (the z axis). These invariances are, of course, caused by the spherical symmetry of the potential of any atom. This additional symmetry of the potential causes the Hamiltonian to commute with all three components of the electron's angular momentum:

- $[L_x, H] = 0$
- $[L_y, H] = 0$
- $[L_z, H] = 0$

It is straightforward to show that H also commutes with the operator L^2, defined as the sum of the squares of the three individual components of the angular momentum

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

Because L_x, L_y, and L_z do not commute with one another, orbitals which are eigenfunctions of H **cannot** be simultaneous eigenfunctions of all three angular momentum operators. However, because L_x, L_y, and L_z do commute with L^2, orbitals can be found which are eigenfunctions of H, of L^2 and of any one component of **L**; it is convention to select L_z as the operator which, along with H and L^2, form a mutually commutative operator set of which the orbitals are simultaneous eigenfunctions.

So, for any atom, the orbitals can be labeled by both l and m quantum numbers, which play the role that point group labels did for non-linear molecules and λ did for linear molecules. Because (i) the kinetic energy operator in the electronic Hamiltonian explicitly contains $\frac{L^2}{2m_e r^2}$, (ii) the Hamiltonian does not contain additional L_z, L_x, or L_y factors, and (iii) the potential energy part of the Hamiltonian is spherically symmetric (and commutes with L^2 and L_z), the energies of atomic orbitals depend upon the l quantum number and are independent of the m quantum number. This is the source of the 2l+1- fold degeneracy of atomic orbitals.

The angular part of the atomic orbitals is described in terms of the spherical harmonics $Y_{l,m}$; that is, each atomic orbital ϕ can be expressed as

$$\phi_{n,l,m} = Y_{l,m}(\theta, \varphi) R_{n,l}(r).$$

The explicit solutions for the Yl,m and for the radial wavefunctions $R_{n,l}$ are given in Appendix B. The variables r, θ, φ give the position of the electron in the orbital in spherical coordinates. These angular functions are, as discussed earlier, related to the cartesian (i.e., spatially oriented) orbitals by simple transformations; for example, the orbitals with l=2 and m=2,1,0,-1,-2 can be expressed in terms of the $d_{xy}, d_{xz}, d_{yz}, d_{xx-yy}$, and d_{zz} orbitals. Either set of orbitals is acceptable in the sense that each orbital is an eigenfunction of H; transformations within a degenerate set of orbitals do not destroy the Hamiltonian- eigenfunction feature. The orbital set labeled with l and m quantum numbers is most useful when one is dealing with isolated atoms (which have spherical symmetry), because m is then a valid symmetry label, or with an atom in a local environment which is axially symmetric (e.g., in a linear molecule) where the m quantum number remains a useful symmetry label. The cartesian orbitals are preferred for describing an atom in a local environment which displays lower than axial symmetry (e.g., an atom interacting with a diatomic molecule in C_{2v} symmetry).

The radial part of the orbital $R_{n,l}$(r) as well as the orbital energy $\varepsilon_{n,l}$ depend on l because the Hamiltonian itself contains $\frac{l(l+1)\hbar^2}{2m_e r^2}$; they are independent of m because the Hamiltonian has no m-dependence. For bound orbitals, $R_{n,l}$(r) decays exponentially for large r (as $e^{-2r\sqrt{2\varepsilon_{n,l}}}$), and for unbound (scattering) orbitals, it is oscillatory at large r with an oscillation period related to the deBroglie wavelength of the electron. In $R_{n,l}$ (r) there are (n-l-1) radial nodes lying between r=0 and $r = \infty$. These nodes provide differential stabilization of low-l orbitals over high-l orbitals of the same principal quantum number n. That is, penetration of outer shells is greater for low-l orbitals because they have more radial nodes; as a result, they have larger amplitude near the atomic nucleus and thus experience enhanced attraction to the positive nuclear charge.

The average size (i.e., $\langle r \rangle$:

$$\langle r \rangle = \int R_{n,l}^2 r r^2 dr)$$

of an orbital depends strongly on n, weakly on l and is independent of m. It also depends strongly on the nuclear charge and on the potential produced by the other electrons. This potential is often characterized qualitatively in terms of an effective nuclear charge Z_{eff} which is the true nuclear charge of the atom Z minus a screening component Z_{sc} which describes the repulsive effect of the electron density lying radially inside the electron under study. Because, for a given n, low-l orbitals penetrate closer to the nucleus than do high-l orbitals, they have higher Z_{eff} values (i.e., smaller Z_{sc} values) and correspondingly smaller average sizes and larger binding energies.