

The Hydrogen Atom Orbitals B

In Chapter 1 and Appendix A, the angular and radial parts of the Schrödinger equation for an electron moving in the potential of a nucleus of charge Z were obtained. These "hydrogen-like" atomic orbitals are proper eigenstates for H, He⁺, Li⁺⁺, Be⁺⁺⁺, etc. They also serve as useful starting points for treating many-electron atoms and molecules in that they have been found to be good basis functions in terms of which to expand the orbitals of most atoms and ions. In this Appendix, we will examine the sizes, energies, and shapes of these orbitals and consider, in particular, how these properties vary with principal quantum number n , charge Z , and angular quantum numbers l and m .

In Chapter 1 and Appendix A, it was shown that the total r, θ, ϕ dependence of these so-called hydrogenic orbitals is given as:

$$\psi_{n,l,m} = Y_{l,m}(\theta, \phi) R_{n,l}(r),$$

where the spherical harmonics $Y_{l,m}$ are expressed in terms of the associated Legendre polynomials $P_l^m(\cos \theta)$ as

$$Y_{l,m}(\theta, \phi) = P_l^{|m|}(\cos \theta) (2\pi)^{-1/2} \exp(im\phi),$$

and the radial functions $R_{n,l}(r)$ are given in terms of Laguerre polynomials of order $n-l-1$, $L_{n-l-1}(\rho)$ as follows:

$$R_{n,l}(r) = N_{n,l}^{-1} e^{-\rho/2} L_{n-l-1}(\rho),$$

where $N_{n,l}$ is a normalization constant. Here, the radial coordinate r of the electron is contained in the variable ρ defined as

$$\rho = Zr/a_0n,$$

where a_0 is the Bohr radius

$$a_0 = \hbar^2 / \mu e^2 = 0.529 \text{ \AA}.$$

The energies of these hydrogenic orbitals, relative to an electron infinitely far from the nucleus and with zero kinetic energy, are

$$E = -\mu Z^2 e^4 / 2\hbar^2 n^2 = -27.21 Z^2 / 2n^2 \text{ eV}.$$

The $n = 1, 2,$ and 3 wavefunctions are given explicitly as follows:

$$\begin{aligned}
 n=1, l=0, m=0, &= (Z/a_0)^{3/2} ()^{-1/2} \exp(-Zr/a_0) \\
 n=2, l=0, m=0, &= (Z/a_0)^{3/2} (2)^{-1/2} (1-Zr/2a_0)/2 \exp(-Zr/2a_0) \\
 n=2, l=1, m=0, &= (Z/a_0)^{3/2} (2)^{-1/2} Zr/4a_0 \cos \exp(-Zr/2a_0) \\
 n=2, l=1, m=\pm 1, &= (Z/a_0)^{3/2} (4)^{-1/2} Zr/4a_0 \sin \exp(\pm i) \exp(-Zr/2a_0) \\
 n=3, l=0, m=0, &= (Z/a_0)^{3/2} (3)^{-1/2} [27-18Zr/a_0+2(Zr/a_0)^2]/81 \\
 &\exp(-Zr/3a_0) \\
 n=3, l=1, m=0, &= (Z/a_0)^{3/2} (2)^{-1/2} 2/81 [6Zr/a_0-(Zr/a_0)^2] \cos \\
 &\exp(-Zr/3a_0) \\
 n=3, l=1, m=\pm 1, &= (Z/a_0)^{3/2} ()^{-1/2} 1/81 [6Zr/a_0-(Zr/a_0)^2] \sin \exp(\pm i) \exp(-Zr/3a_0) \\
 n=3, l=2, m=0, &= (Z/a_0)^{3/2} (6)^{-1/2} 1/81 (Zr/a_0)^2 [3\cos^2 -1] \\
 &\exp(-Zr/3a_0) \\
 n=3, l=2, m=\pm 1, &= (Z/a_0)^{3/2} ()^{-1/2} 1/81 (Zr/a_0)^2 \sin \cos \exp(\pm i) \exp(-Zr/3a_0) \\
 n=3, l=2, m=\pm 2, &= (Z/a_0)^{3/2} (4)^{-1/2} 1/81 (Zr/a_0)^2 \sin^2 \exp(\pm 2i) \exp(-Zr/3a_0).
 \end{aligned}$$

On pages 133-136 of Pauling and Wilson are tabulated the bound-state solutions of this problem for n ranging up to $n=6$ and l -values up to $l=5$.

The above $\pm m$ functions are appropriate whenever one wishes to describe orbitals that are eigenfunctions of L_z , the component of orbital angular momentum along the z -axis. The functions with $\pm m$ quantum numbers can be combined in pairs to give the spatially oriented functions with which most chemists are familiar:

$$+ = 2^{-1/2} [\psi_{m+} + \psi_{-m}]$$

and

$$- = 2^{-1/2} [\psi_{m-} - \psi_{-m}].$$

For example, when applied to the $2p_{\pm 1}$ functions, one forms the $2p_x$ and $2p_y$ functions; the $3d_{\pm 1}$ functions combine to give the $3d_{xz}$ and $3d_{yz}$ functions; and the $3d_{\pm 2}$ functions combine to give the $3d_{xy}$ and $3d_{x^2-y^2}$ functions. These spatially directed functions are more appropriate for use whenever one is dealing with the interaction of the atom on which these orbitals are located with surrounding "ligands" or bonding partners which are spatially arranged in a manner that destroys the spherical and axial symmetry of the system. One is permitted to combine the $\pm m$ functions in this manner because these pairs of functions are energetically degenerate; any combination of them is therefore of the same energy.

There are several important points to stress about these hydrogenic atomic functions:

1. Their energies vary as $-Z^2/n^2$, so atoms with higher Z values will have more tightly bound electrons (for the same n). In a many-electron atom, one often introduces the concept of an effective nuclear charge Z_{eff} , and takes this to be the full nuclear charge Z minus the number of electrons that occupy orbitals that reside radially "inside" the orbital in question. For example, $Z_{\text{eff}} = 6-2=4$ for the $n=2$ orbitals of Carbon in the $1s^2 2s^2 2p^4$

configuration. This Z_{eff} is then used to qualitatively estimate the relative energetic stability by making use of the $-Z_{\text{eff}}^2/n^2$ scaling of the energy.

2. The radial sizes of orbitals are governed by the product of $\exp(-Z_{\text{eff}} r/n a_0)$, an r^l factor which arises from the small- r limit of $\psi_{n,l,m}$, r^l which enters because the probability density is $|\psi|^2 r^2$, and the highest power of $Zr/n a_0$ that appears in the Laguerre polynomial which is $(Zr/n a_0)^{n-l-1}$. This product's r -dependence reduces to $\exp(-Z_{\text{eff}} r/n a_0) r^n$, which has a maximum at $r = n^2 a_0/Z_{\text{eff}}$. So, orbitals with large Z_{eff} values are smaller and orbitals with larger n -values are larger.

3. The hydrogenic atom energy expression has no l -dependence; the 2s and 2p orbitals have exactly the same energy, as do the 3s, 3p, and 3d orbitals. This degree of degeneracy is only present in one-electron atoms and is the result of an additional symmetry (i.e., an additional operator that commutes with the Hamiltonian) that is not present once the atom contains two or more electrons. This additional symmetry is discussed on p. 77 of Atkins.

4. The radial part of $\psi_{n,l,m}$ involves a polynomial in r of order $n-l-1$

$$L_{n-l-1}(r) = \sum_k a_k r^k,$$
and the coefficients in these polynomials alternate in sign ($a_k = c_k (-1)^k$). As a result, the radial functions possess nodes (i.e., values of r at which $\psi_{n,l,m}$ vanishes) at points where the polynomial is equal to zero. There are $n-l-1$ such radial nodes (excluding the nodes at $r = \infty$ and at $r = 0$, the latter of which all but s-orbitals have). A 4s orbital has 3 such radial nodes, and a 3d orbital has none. Radial nodes provide a means by which an orbital acquires density closer to the nucleus than its $\langle r^2 \rangle$ value would indicate; such enhanced density near the nucleus differentially stabilizes such orbitals relative to those with the same n but fewer nodes. In the language commonly used in inorganic chemistry, one says that nodes allow an orbital to "penetrate" the underlying inner-shell orbitals.

The presence of radial nodes also indicates that the electron has radial kinetic energy. The 3s orbital with 2 radial nodes has more radial kinetic energy than does the 3p which, in turn, has more than the 3d. On the other hand, the 3d orbital has the most angular energy

$l(l+1)\hbar^2/2mr^2$ (this is the analog of the rotational energy of a diatomic molecule), the 3p has an intermediate amount, and the 3s has the least.