

CHAPTER OVERVIEW

20: The Hydrogen Atom

In this chapter we will consider the hydrogen atom as a proton fixed at the origin, orbited by an electron of reduced mass μ . The potential due to electrostatic attraction is:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}, \quad (20.1)$$

where ϵ_0 is the constant permittivity of vacuum. The kinetic energy term in the Hamiltonian is

$$K = -\frac{\hbar^2}{2\mu} \nabla^2, \quad (20.2)$$

where ∇^2 is the Laplace operator (*Laplacian*) representing the divergence of the gradient of a function. Recall that in 1-dimension the kinetic energy is proportional to the second derivative of the wave function with respect to the position. In 3-dimension, the first derivative along all three dimension of space is called gradient, which is written in cartesian coordinates $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right)$. The Laplacian is the divergence $\nabla \cdot$ of the gradient (effectively, it replaces the second derivatives in the 1-D case), and can be written in cartesian coordinates as $\nabla^2 = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. The TISEq for the Hydrogen atom is therefore:

$$\left(-\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi(r, \theta, \phi) = E\psi(r, \theta, \phi), \quad (20.3)$$

which, replacing the Laplacian in spherical coordinates, becomes:

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{e^2}{4\pi\epsilon_0 r} \psi = E\psi. \quad (20.4)$$

This equation seems very complicated, but comparing the term in between square brackets with the TISEq of the rigid rotor, we immediately see some connections. Equation 20.4 is a separable, partial differential equation that can be solved by factorizing the wave function $\psi(r, \theta, \phi)$ into $R_{nl}(r)Y_\ell^{m_\ell}(\theta, \phi)$, where $Y_\ell^{m_\ell}(\theta, \phi)$ are again the spherical harmonics that solved the TISEq for the rigid rotor. The radial part $R(r)$ obeys the equation:

$$-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) \left[\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} + V(r) - E \right] R(r) = 0, \quad (20.5)$$

which is called the radial equation for the hydrogen atom. The solutions of the radial part are:

$$R_{n\ell}(r) = - \left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right]^{1/2} \left(\frac{2}{na_0} \right)^{\ell+3/2} r^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1} \left(\frac{2r}{na_0} \right) \quad (20.6)$$

where $0 \leq \ell \leq n-1$, and $a_0 = \frac{\epsilon_0 \hbar^2}{\pi \mu e^2}$ is the Bohr radius. The functions $L_{n+\ell}^{2\ell+1} \left(\frac{2r}{na_0} \right)$ are the associated Laguerre functions.

The hydrogen atom eigenfunctions are:

$$\begin{aligned} \psi_{n\ell m_\ell}(r, \theta, \phi) &= R_{n\ell}(r) Y_\ell^{m_\ell}(\theta, \phi) = \\ &= - \left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3} \right]^{1/2} \left(\frac{2}{na_0} \right)^{\ell+3/2} r^\ell e^{-r/na_0} L_{n+\ell}^{2\ell+1} \left(\frac{2r}{na_0} \right) Y_\ell^{m_\ell}(\theta, \phi) \end{aligned}$$

The quantum numbers n, ℓ, m_ℓ can take the following values:

- $n = 1, 2, 3, \dots, \infty$ (principal quantum number),
- $\ell = 0, 1, 2, \dots, n-1$ (azimuthal quantum number),

- $m_\ell = -\ell, \dots, \ell$ (magnetic quantum number).

These functions are called the *hydrogen atom orbitals*, and are usually first encountered in introductory chemistry textbooks. Notice that—by definition—an orbital is a complex function (i.e., it has both a real and an imaginary component) that describes *exclusively* one electron. Spherical harmonics are orthogonal to each other and they can be linearly combined to form new solutions to the TISEq where the imaginary part is removed. (Because of the orthogonality of spherical harmonics, the energy spectrum will not be affected by this operation.) These corresponding real orbitals are three-dimensional functions that are not easily visualized in a three-dimensional space, since they require a four-dimensional one.¹ Since there is no real consensus on what a wave function represents, the interpretation of orbitals is not straightforward.² We will return to the interpretation problem in future chapters, but for now it is important to keep in mind these following facts:

- The shape of every hydrogen atom orbital—complex or real—is that of a function on the surface of a sphere (yes, this is true for every single one of them, since they all come from spherical harmonics, which are special functions defined on the surface of a sphere. Hydrogen $2p$ orbitals in real space *do not* have the shape of a dumbbell, as often is said in general chemistry textbooks. Same goes for d, f, \dots orbitals.)
- Each orbital is the mathematical description of one—and only one—electron (in other words, orbitals do not “contain” electrons, they “are” the functions that describe each electron.)
- Hydrogen orbitals are defined only for systems that contain one electron. When more than one electron is present in an atom, the TISEq in Equation 20.3 does not describe the system anymore. In these more complicated situations the TISEq cannot be solved analytically, and orbitals cannot be easily defined (we will see in [chapter 26](#) how we can circumvent this issue in an approximate manner, and why general chemistry textbooks talk of orbitals for every atom and molecule.)

The hydrogen atom eigenvalues are:

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \quad n = 1, 2, \dots, \infty. \quad (20.7)$$

Notice how the eigenvalues (i.e., the energy spectrum) do not depend on the azimuthal and magnetic quantum numbers, ℓ and m . Energy levels with the same n , but different ℓ and/or m are called *degenerate states*, since they all have the same energy. This is, once again, source of misinterpretation in most general chemistry textbooks:

- According to the TISEq, the $2s$ and $2p$ orbitals of the hydrogen atom have the same energy.³

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1. If it is not clear why you need a 4-D space to visualize a 3-D function, think at the fact that we use a 2-D space (the Cartesian plane) to visualize a 1-D function ($f(x)$).
 2. At least not as straightforward as it is given in introductory chemistry textbooks.
 3. In practice, this is not true, because of a tiny effect called the [Lamb shift](#). The description of this effect requires to go beyond the Schrödinger equation—and essentially beyond quantum mechanics—into the field of quantum electrodynamics. The Lamb shift, however, is not what is usually depicted in general chemistry textbooks as the $2s - 2p$ energy difference. The difference that is usually discussed in the context of the aufbau principle is a many-electron effect, as we will discuss in chapter 10, and does not apply to hydrogen.

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