The Richard Stockton College of New Jersey
Chemistry Program, School of Natural Sciences and Mathematics
PO Box 195, Pomoma, NJ

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 10: The Hydrogen Atom

References

1. Levine, *Physical Chemistry*, Sections 18.1–18.4
2. Hydrogen atom handout

Key Concepts

- To solve the Schrödinger Equation for the hydrogen atom we need to write the potential energy of the electron as

$$V = \frac{-Ze^2}{r}$$

  where Z is the number of protons, e is the elementary charge, and r is the radial distance between the electron and nucleus. Several constants have been left out of the above expression.

- Because of the symmetry of atomic structure and V depends on r, spherical coordinates need to be used to describe atomic structure. In spherical coordinates there parameters are used to describe the position of a point in space: r, the radial distance from the origin, θ, angle between r and the z-axis, and ϕ the angle measured from the x-axis.

- When we switch to spherical coordinates, the Laplacian operator (∇^2) changes as well:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

- Combining this with the Schrödinger Equation and separating variables such that $\Psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$ we get:

$$\frac{\Theta\Phi}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R\Phi}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{R\Theta}{r^2\sin^2\theta}\frac{d^2\Phi}{d\phi^2} + \frac{2m_eZe^2}{\hbar^2 r}R\Theta\Phi + \frac{2mE}{\hbar^2}R\Theta\Phi = 0$$

- With a little housekeeping we can separate the Φ terms from the R and Θ terms:

$$\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{2m_eZe^2}{\hbar^2}r + \frac{2m_eE}{\hbar^2}r^2\right]\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2$$

- This give us familiar solutions for $\Phi(\phi)$ in the form:

$$\Phi(\phi) = \begin{cases} e^{im\phi} \\ e^{-im\phi} \end{cases}$$

  This solution represents one third of the overall solution for Ψ. In solving for $\Phi(\phi)$ the quantum number m, also known as the magnetic quantum number, naturally appears.

- If we do a little more rearranging we can get an equation that only involves θ terms:

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\lambda\sin^2\theta - m^2\right)\Theta = 0$$

  which is the Legendre equitation. Solutions exist for this equation in the form:

$$\Theta_{lm}(\theta) = \Theta_l^m(\theta) = P_l^m(\cos\theta)$$

  where $P_l^m(\cos\theta)$ is defined in the handout distributed in class.

- The solution of the θ part of Ψ introduces another quantum number, l, often called the angular momentum quantum number.