

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 12: Radial distribution function, spectra, and beyond

References

1. Levine, *Physical Chemistry*, Sections 18.1–18.5

Key Concepts

- To understand the electron distribution in the hydrogen atom we need to focus on probability and not simply the solutions to the Schrödinger Equation. Just like when we looked at the PIB, Ψ^2 was more important than Ψ .
- In the case of the 3-D solutions for hydrogen, the quantity we are interested is not just Ψ^2 , which will tell us something about the probability of being at a particular point in space. We are more interested in the probability of finding electrons at a certain distance from the origin (nucleus).
- The radial distribution function (rdf), $P(r)$, gives us this probability.

$$P(r) \propto r^2 R^2$$

So the quantity we are interested is not just R^2 but the product of $r^2 R^2$. This takes into account the increased number of states as r increases.

- The solutions to the Schrödinger Equation now provide some physical insight into some of the pre-QM empirical observations of Balmer and Rydberg. Both were able to fit their experimental observations of the hydrogen emission spectrum to the following relationship:

$$\frac{1}{\lambda} = R_y \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where R_y is an empirical constant and n_f and n_i are integers that fit particular lines in the spectrum.

- The QM solutions for the hydrogen wave functions give the same expression but the constant R_y is a set of physical constants with meaning and the integers n_f and n_i indicate transitions from one quantum state to another.
- The solutions for the hydrogen orbitals also introduce degenerate states for $n > 1$. These states have multiple solutions to the Schrödinger Equation, each with the same energy E_n . One would expect all transitions to be possible, but the transitions are limited $\Delta l = \pm 1$. This is an example of a selection rule that determines which transitions are allowed and which are “forbidden.”
- The picture of the hydrogen atom obtained from the Schrödinger Equation fits with observed spectra and explains why splitting is observed in spectra obtained from samples under an applied magnetic field. For wave functions with $l \neq 0$, an applied magnetic field changes the relative energies of the orbitals and leads to multiple spectral lines.