

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 15: Applications to atomic spectroscopy

## References

1. Levine, *Physical Chemistry*, Sections 18.5–7

## Key Concepts

- We have developed a sophisticated model of atomic structure of both hydrogen-like and multi-electron atoms. The question is how can we use this model to understand observed properties of atoms.
- Atomic spectroscopy is one example of a place where we can relate our understanding of atomic structure to observed properties.
- We have already begun to do this in trying to understand atomic spectra. For example, we have used our quantum mechanical model to understand the reason behind observed spectra.
- We can add some more to this picture by looking at selection rules a bit more closely:
  - describe which electronic transitions we would expect to observe in atomic spectroscopy
  - Quantitatively related to the transition probability,  $p_{nm}$ , which is the probability of a transition from the  $n$  to the  $m$  state. This is given by:

$$p_{nm} = \int \Psi_m^* \hat{p} \Psi_n d\tau$$

where  $\hat{p}$  is the electronic dipole operator, and  $\Psi$  represents the wave function of the indicated level. If one were to do this integral,  $d\tau$  indicates we need to do it over all possible electronic states.

- The intensity of an observed spectral line is proportional to the transition probability. For transitions where  $p_{nm} \approx 0$ , the transition is forbidden, i.e. it is not observed. For non-zero transition probability we say the transition is allowed or observed.
- We can derive the familiar form of Beer's Law by accounting for the change in light intensity as it travels through a sample.

$$\log \frac{I_{\lambda_o}}{I_{\lambda}} = \frac{a_{\lambda}}{2.303} cl \rightarrow Abs = \epsilon_{\lambda} cl$$

where  $I_{\lambda_o}$  is the incident light intensity,  $I_{\lambda}$  is the transmitted intensity,  $c$  is the concentration,  $l$  is the path length, and  $\epsilon_{\lambda}$  is the molar extinction coefficient.

- All of the quantum mechanical information (i.e. information about atomic structure) is contained within the extinction coefficient.
  - is there a transition of an energy equal to the incoming energy?
  - what is the transition probability of the transition that could be excited by the incident energy?
- Through the extinction coefficient we see the atomic structure manifest in observable properties.