

## 8.3: Orbital Energy Levels, Selection Rules, and Spectroscopy

The orbital energy eigenvalues obtained by solving the hydrogen atom Schrödinger equation are given by

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \quad (8.3.1)$$

where  $\mu$  is the reduced mass of the proton and electron,  $n$  is the principal quantum number and  $e$ ,  $\epsilon_0$  and  $h$  are the usual fundamental constants. The energy is negative and approaches zero as the quantum number  $n$  approaches infinity. Because the hydrogen atom is used as a foundation for multi-electron systems, it is useful to remember the total energy (binding energy) of the ground state hydrogen atom,  $E_H = -13.6 \text{ eV}$ . The spacing between electronic energy levels for small values of  $n$  is very large while the spacing between higher energy levels gets smaller very rapidly. This energy level spacing is a result of the form of the Coulomb potential, and can be understood in terms of the particle in a box model. We saw that as the potential box gets wider, the energy level spacing gets smaller. Similarly in the hydrogen atom as the energy increases, the Coulomb well gets wider and the energy level spacing gets smaller.

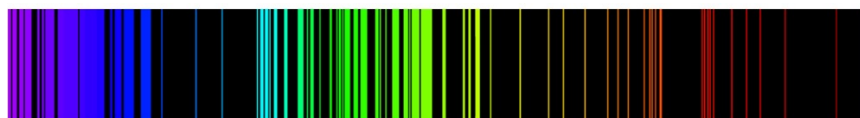


Figure 8.3.1: the emission line spectrum for iron. The discrete lines imply quantized energy states for the atoms that produce them.

The line spectra produced by hydrogen atoms are a consequence of the quantum mechanical energy level expression, Equation 8.3.1. In Chapter 1 we saw the excellent match between the experimental and calculated spectral lines for the hydrogen atom using the Bohr expression for the energy, which is identical to Equation 8.3.1.

### Exercise 8.3.1

Using Equation 8.3.1 and a spreadsheet program or other software of your choice, calculate the energies for the lowest 100 energy levels of the hydrogen atom. Also calculate the differences in energy between successive levels. Do the results from these calculations confirm that the energy levels rapidly get closer together as the principal quantum number  $n$  increases? What happens to the energy level spacing as the principle quantum number approaches infinity?

The solution of the Schrödinger equation for the hydrogen atom predicts that energy levels with  $n > 1$  can have several orbitals with the same energy. In fact, as the energy and  $n$  increase, the degeneracy of the orbital energy level increases as well. The number of orbitals with a particular energy and value for  $n$  is given by  $n^2$ . Thus, each orbital energy level is predicted to be  $n^2$ -degenerate. This high degree of orbital degeneracy is predicted only for one-electron systems. For multi-electron atoms, the electron-electron repulsion removes the  $l$  degeneracy so only orbitals with the same  $m_l$  quantum numbers are degenerate.

### Exercise 8.3.2

Use Equation or the data you generated in Exercise 8.3.1 to draw an energy level diagram to scale for the hydrogen atom showing the first three energy levels and their degeneracy. Indicate on your diagram the transition leading to ionization of the hydrogen atom and the numerical value of the energy required for ionization, in eV, atomic units and kJ/mol.

To understand the hydrogen atom spectrum, we also need to determine which transitions are allowed and which transitions are forbidden. This issue is addressed next by using selection rules that are obtained from the transition moment integral. In previous chapters we determined selection rules for the particle in a box, the harmonic oscillator, and the rigid rotor. Now we will apply those same principles to the hydrogen atom case by starting with the transition moment integral.

The transition moment integral for a transition between an initial ( $i$ ) state and a final ( $f$ ) state of a hydrogen atom is given by

$$\langle \mu_T \rangle = \int \psi_{n_f, l_f, m_{l_f}}^*(r, \theta, \psi) \hat{\mu} \psi_{n_i, l_i, m_{l_i}}(r, \theta, \psi) d\tau \quad (8.3.2)$$

or in bra ket notation

$$\langle \mu_T \rangle = \langle \psi_{n_f, l_f, m_{l_f}}^* | \hat{\mu} | \psi_{n_i, l_i, m_{l_i}} \rangle \quad (8.3.3)$$

where the dipole moment operator is given by

$$\hat{\mu} = -e\hat{r} \quad (8.3.4)$$

The dipole moment operator expressed in spherical coordinates is

$$\hat{\mu} = -er(\bar{x} \sin \theta \cos \psi + \bar{y} \sin \theta \sin \psi + \bar{z} \cos \theta) \quad (8.3.5)$$

The sum of terms on the right hand side of Equation 8.3.5 shows that there are three components of  $\langle \mu_T \rangle$  to evaluate in Equation 8.3.2, where each component consists of three integrals: an  $r$  integral, a  $\theta$  integral, and a  $\psi$  integral.

Evaluation reveals that the  $r$  integral **always differs** from zero so

$$\Delta n = n_f - n_i = \text{not restricted} \quad (8.3.6)$$

There is no restriction on the change in the principal quantum number during a spectroscopic transition;  $\Delta n$  can be anything. For absorption,  $\Delta n > 0$ , for emission  $\Delta n < 0$ , and  $\Delta n = 0$  when the orbital degeneracy is removed by an external field or some other interaction.

The selection rules for  $\Delta l$  and  $\Delta m_l$  come from the transition moment integrals involving  $\theta$  and  $\varphi$  in Equation 8.3.2. These integrals are the same ones that were evaluated for the rotational selection rules, and the resulting selection rules are

$$\Delta l = \pm 1 \quad (8.3.7)$$

and

$$\Delta m_l = 0, \pm 1 \quad (8.3.8)$$

### Exercise 8.3.3

Write the spectroscopic selection rules for the rigid rotor and for the hydrogen atom. Why are these selection rules the same?

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