# Physics GRE:

# Atomic Physics


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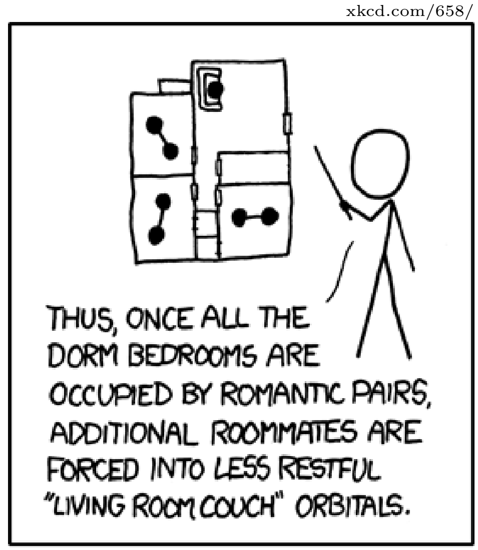


THE PAULI SEXCLUSION PRINCIPLE

# Contents

# 1 Bohr Model

The Bohr model of the atom was proposed in 1913 and rests on several assumptions:

- Electrons circle the nucleus in stable orbits.
- The orbits occur at discrete radii and have discrete energies associated with them.
- Electrons gain or lose energy by switching between orbits, absorbing or emitting photons with a frequency $\nu$ related to the energy difference, $\Delta E = h\nu$, where $h$ is Planck's constant.

Using these assumptions Bohr was able to show the angular momentum was quantized; namely, it was an integer multiple of the reduced Planck constant:

$$L = n\hbar \qquad n \in \{1, 2, 3, \ldots\} \tag{1}$$

For $n = 1$ this corresponds to the smallest orbit, with radius $a_0 = 0.529\,\text{Å}$, the so-called "Bohr radius". The model explained why atoms were stable and accurately predicted the atomic spectrum for Hydrogen. However, it did not generalize to other atomic species and so was clearly not a complete theory.

The radius of the $n^{\text{th}}$ orbit is

$$r_n = \frac{\hbar^2 n^2}{Zke^2\mu} = \frac{a_0 n^2}{Z} \tag{2}$$

The energy of the $n^{\text{th}}$ level is

$$E_n = -\frac{Zke^2}{2r_n} = -\frac{\mu Z^2 k^2 e^4}{2\hbar^2 n^2} = -\frac{1}{2}\mu c^2 \frac{Z^2\alpha^2}{n^2} \approx -13.6\,\text{eV}\frac{Z^2}{n^2} \tag{3}$$

When an electron makes a transition a photon is released with energy and wavelength given by

$$E = \frac{hc}{\lambda} = 13.6\,\text{eV}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \tag{4}$$

Transitions in which the electron ends in a fixed level are given names: $n_f = 1$ is the Lyman series, $n_f = 2$ is the Balmer series and $n_f = 3$ is the Paschen series. These correspond to wavelengths which fall in different regions of the EM spectrum. Considering transitions with initial states between $n_i = n_f + 1$ and $n_i \to \infty$ give the ranges

$$\text{Lyman: } n_f = 1 \qquad 90\,\text{nm} < \lambda < 120\,\text{nm} \tag{5}$$

$$\text{Balmer: } n_f = 2 \qquad 360\,\text{nm} < \lambda < 660\,\text{nm} \tag{6}$$

$$\text{Paschen: } n_f = 3 \qquad 820\,\text{nm} < \lambda < 1880\,\text{nm} \tag{7}$$

Note that the Blamer series falls within the visible part of the EM spectrum.

# 2 Atomic Structure

The states for electrons in atoms are labeled by quantum numbers; the principle quantum number $n$, the azimuthal quantum number $l$, the magnetic quantum number $m_l$ and the spin projection quantum number $m_s$. The possible values for these quantum labels are

$$n \in \{1, 2, 3, \ldots\} \qquad l \in \{0, 1, \ldots, n-1\} \qquad m_l \in \{-l, -l+1, \ldots, l\} \qquad m_s \in \{-s, -s+1, \ldots, s\} \tag{8}$$

For electrons, $s = \frac{1}{2}$, and so $m_s$ can have one of two values: $m_s = \pm\frac{1}{2}$. The values of $l$ are given names: $l = 0$ is denoted $S$, $l = 1$ is $P$, $l = 2$ is $D$, $l = 3$ is $F$, &c.

Spectroscopic notation displays an atomic state with spin angular momentum $\boldsymbol{S}$, orbital angular momentum $\boldsymbol{L}$ and total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$:

$$^{2S+1}L_J \tag{9}$$

$2S + 1$ is the multiplicity of the state. For example, the ground state of Hydrogen is $^2\mathrm{S}_{1/2}$, the ground state of Helium is $^1\mathrm{S}_0$ and the ground state of Boron is $^2\mathrm{P}_{1/2}$.

## 3 Selection Rules

Electric dipole selection rules give criteria for transitions to occur through spontaneous emission of a photon in an atom. The probability of a transition is proportional to

$$P(i \to f) \propto \langle \psi_i | \boldsymbol{r} | \psi_f \rangle \tag{10}$$

The computation of these matrix elements is quite involved, so we will only quote the result. For a transition to be allowed, the quantum numbers associated with the initial and final states must be related by

$$\Delta l = \pm 1 \qquad \Delta m = 0, \pm 1 \qquad \Delta s = 0 \qquad j_i = 0 \not\to j_f = 0 \tag{11}$$

Other transitions are allowed, but with probabilities smaller by a factor of $\alpha^2$.

## 4 Blackbody Radiation

Throughout the $19^{\text{th}}$ century a consistent description of blackbody radiation was nonexistant. The theory was plagued by an "ultraviolet catastrophe" and descriptions of high or low wavelength only made sense in their respective domains. The unifying equation, known as Planck's law, relies on quantization of energy in its derivation. Wien's displacement law gives the location of the peak of this distribution. These two laws are:

$$I_{\mathrm{P}}(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \qquad \lambda_{\text{peak}} T = 2.9 \cdot 10^6 \,\mathrm{nm\,K} \tag{12}$$

The high and low wavelength approximations are the Raleigh-Jeans law and Wien's law, respectively.

$$I_{\mathrm{RJ}}(\lambda, T) = \frac{2ckT}{\lambda^4} \qquad I_{\mathrm{W}}(\lambda, T) = \frac{2hc^2}{\lambda^5} e^{-\frac{hc}{\lambda kT}} \tag{13}$$

Another important piece in describing blackbody radiation is the Stefan-Boltzmann law, which gives that the power radiated per unit time is proportional to $T^4$.

## 5 Compton Scattering

When a photon scatters off of a charged particle it imparts some of its energy, increasing its wavelength. Often the charged particle is an electron. We have both energy and momentum conservation, and so, in the frame where the charged particle is initially at rest, we have

$$E_{\gamma i} + E_i = E_{\gamma f} + E_f \qquad \boldsymbol{p}_{\gamma i} = \boldsymbol{p}_{\gamma f} + \boldsymbol{p}_f \tag{14}$$

where the $\gamma$ subscript denotes quantities pertaining to the photon. Using the relativistic energy formula, we have

$$p_{\gamma i}c + mc^2 = p_{\gamma f}c + \sqrt{(mc^2)^2 + (p_f c)^2} \qquad \boldsymbol{p}_f \cdot \boldsymbol{p}_f = (\boldsymbol{p}_{\gamma i} - \boldsymbol{p}_{\gamma f}) \cdot (\boldsymbol{p}_{\gamma i} - \boldsymbol{p}_{\gamma f}) \tag{15}$$

$$(mc^2)^2 + (p_f c)^2 = (p_{\gamma i}c - p_{\gamma f}c + mc^2)^2 \qquad p_f^2 = p_{\gamma i}^2 + p_{\gamma f}^2 - 2p_{\gamma i}p_{\gamma f}\cos\theta \tag{16}$$

$$p_f^2 = p_{\gamma i}^2 + p_{\gamma f}^2 - 2p_{\gamma i}p_{\gamma f} + 2(p_{\gamma i} - p_{\gamma f})mc \tag{17}$$

The angle $\theta$ is measured between the incoming and outgoing trajectories of the photon. Combining these two equations by eliminating $p_f$ results in

$$-2p_{\gamma i}p_{\gamma f} + 2(p_{\gamma i} - p_{\gamma f})mc = -2p_{\gamma i}p_{\gamma f}\cos\theta \tag{18}$$

$$\frac{1}{p_{\gamma f}} - \frac{1}{p_{\gamma i}} = \frac{1}{mc}(1 - \cos\theta) \tag{19}$$

$$\Delta\lambda = \lambda_f - \lambda_i = \frac{h}{mc}(1 - \cos\theta) \tag{20}$$

The constant $\frac{h}{mc}$ is known as the Compton wavelength, which for an electron has the value

$$\lambda_{\mathrm{C}} = \frac{h}{m_e c} \approx 2.43 \cdot 10^{-3}\,\mathrm{nm} = 2.43\,\mathrm{pm} \tag{21}$$

# 6 Moseley's Law

High energy particles can crash into atoms and kick out one the inner electrons. This gap is quickly filled by an electron in a higher shell, emitting an x-ray photon in the process. The labels $K$, $L$, $M$, &c denote the final state of the transition. For example, $K\alpha$ refers to transitions $n = 2 \to 1$ when an inner-most electron is kicked out. Due to the shielding of inner shells, the energy of the $K\alpha$ photons released is empirically found to follow

$$E = 13.6\,\mathrm{eV} \cdot (Z-1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2}\right) = 13.6\,\mathrm{eV}\left(\frac{3}{4}\right)(Z-1)^2 \tag{22}$$

The $L\alpha$ transitions, $n = 3 \to 1$, are empirically found to satisfy

$$E = 13.6\,\mathrm{eV} \cdot (Z-7.4)^2 \left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 13.6\,\mathrm{eV}\left(\frac{5}{36}\right)(Z-7.4)^2 \tag{23}$$

These results are known as Moseley's law. The constants 1 and 7.4 give a sense of how much the nucleus is shielded by the inner electrons.

# 7 Atoms in Electric & Magnetic Fields

This section relies on knowledge of time-independent perturbation theory. See the quantum mechanic notes for this background information.

**7.1 Stark Effect** Consider plopping a Hydrogen atom into a weak, uniform electric field. We might as well assume that it points along the $z$-axis, so that the perturbing Hamiltonian is

$$H' = e\mathcal{E}z \tag{24}$$

The script $\mathcal{E}$ denotes the electric field strength so as not to be confused with the energy. The mechanism of perturbation theory is only valid for non-degenerate states: in Hydrogen only the ground state. The first order correction to the ground state energy is

$$E_{100}^{(1)} = e\mathcal{E}\,\langle\psi_{100}|z|\psi_{100}\rangle = 0 \tag{25}$$

This vanishes because $z$ is an odd function and the remainder of the integrand is even. One may show that levels for $n \geq 2$ are split symmetrically about their unperturbed energy.

**7.2 Zeeman Effect** What happens to the energy spectrum of Hydrogen when subjected to a weak, uniform magnetic field? Here the perturbing Hamiltonian would be

$$H' = -\boldsymbol{\mu}\cdot\boldsymbol{B} = -\frac{ge}{2m}\boldsymbol{J}\cdot\boldsymbol{B} \tag{26}$$

Assuming that the magnetic field points along the $z$-axis, this becomes

$$H' = -\frac{geB}{2m}J_z \tag{27}$$

The result of this is to split degenerate $l$ levels based on the value of $m_l$, evenly about their unperturbed energy. Roughly, the state will be lower in energy if the angular momentum is aligned with the magnetic field.

# A Summary

### Bohr Model

$$L = n\hbar \qquad n \in \{1, 2, 3, \ldots\} \tag{Quantization Assumption}$$

$$r_n = \frac{\hbar^2 n^2}{Zke^2\mu} = \frac{a_0 n^2}{Z} \tag{Radii}$$

$$a_0 = \frac{\hbar^2}{kme^2} \approx 0.529\,\text{Å} \tag{Bohr Radius}$$

$$E_n = -\frac{Z^2k^2e^4\mu}{2\hbar^2n^2} = -13.6\,\text{eV}\frac{Z^2}{n^2} \tag{Hydrogen Energy Levels}$$

$$n \in \{1, 2, 3, \ldots\} \tag{Principle Quantum Nº}$$

$$l \in \{0, 1, \ldots, n-1\} \tag{Azimuthal Quantum Nº}$$

$$m_l \in \{-l, -l+1, \ldots, l\} \tag{Magnetic Quantum Nº}$$

$$m_s \in \{-s, -s+1, \ldots, s\} \tag{Spin Projection Quantum Nº}$$

### Selection Rules

$$\begin{aligned} \Delta l &= \pm 1 \\ \Delta m &= 0, \pm 1 \\ \Delta s &= 0 \\ j_i = 0 &\not\to j_f = 0 \end{aligned} \tag{Electric Dipole Selection Rules}$$

### Blackbody Radiation

$$I_{\text{P}}(\lambda, T) = \frac{2hc^2}{\lambda^5}\frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \tag{Planck's Law}$$

$$\lambda_{\text{peak}}T = 2.9 \cdot 10^6\,\text{nm K} \tag{Wien's Displacement Law}$$

$$I_{\text{RJ}}(\lambda, T) = \frac{2ckT}{\lambda^4} \tag{Raleigh-Jeans Law}$$

$$I_{\text{W}} = \frac{2hc^2}{\lambda^5}e^{-\frac{hc}{\lambda kT}} \tag{Wien's Law}$$

### Compton Scattering

$$\Delta\lambda = \frac{h}{mc}(1 - \cos\theta) \tag{Compton Shift}$$

$$\lambda_{\text{C}} = \frac{h}{mc} \tag{Compton Wavelength}$$

$$\lambda_{\text{C}} = \frac{h}{m_e c} \approx 2.43\,\text{pm} \tag{Electron Compton Wavelength}$$

### Moseley's Law

$$E = 13.6\,\text{eV}\left(\frac{3}{4}\right)(Z-1)^2 \tag{$K\alpha$ Photons: $n = 2 \to 1$}$$

$$E = 13.6\,\text{eV}\left(\frac{5}{36}\right)(Z-7.4)^2 \tag{$L\alpha$ Photons: $n = 3 \to 2$}$$