CHAP. 28 & 29: PHOTONS, QUANTUM PHYSICS & STRUCTURE OF THE ATOM

In the early 1900s, a number of experiments and important discoveries led toward our 20th-century picture of the overall structure of the atom:

J.J. Thomson: discovery of the e^- & measurement of charge-to-mass (e/m) ratio for e^- (1897)
Robert A. Millikan: measurement of charge of the electron (1910–13)
Ernest Rutherford: existence of a concentrated nucleus (1911)
Discovery of neutron (1932), etc.

Before this, people had thought of atoms as impenetrable, solid little billiard balls; afterward, the atom was seen as having almost all its mass concentrated in **protons** and **neutrons** in a **nucleus**, only 10^{-15} to 10^{-14} m in size, while the **electrons** "orbit" the nucleus at a distance of 10^{-10} to 10^{-9} m, and have $\approx$ 1/1800 the mass of a nucleon. Charge comes in discrete (**quantized**) amounts: the smallest amount of charge in nature is 1.602×10^{-19} C = the charge on an e^- or a p^+.

THERMAL (or "BLACKBODY") RADIATION

Every object (solid, liquid, or a dense gas, like a star) at any T above absolute zero radiates light (EM radiation) *spontaneously* at all wavelengths! The *total luminosity* or *flux* (energy $\div$ surface area, in [W/m^2]) given off by an ideal "**blackbody**" object is:

$$L = \sigma_B T^4$$

Stefan-Boltzmann Law
(σ_B = Stefan-Boltzmann constant
$= 5.671 \times 10^{-8}$ W/m^2·K^4)

Of course, the radiation is *not* of equal intensity at all wavelengths; instead, it diminishes at both high λ and low λ, and peaks at a wavelength λ_{peak}, depending on the blackbody's temperature:

$$\lambda_{peak} = \frac{2.898 \times 10^{-3} \text{ m} \cdot \text{K}}{T}$$

Wien's Law or

Wien's Displacement Law

Therefore: **the hotter the blackbody**, **the shorter the *peak* wavelength** of its blackbody emission. All solid/dense matter in the universe is giving off EM radiation spontaneously right now. Even you!
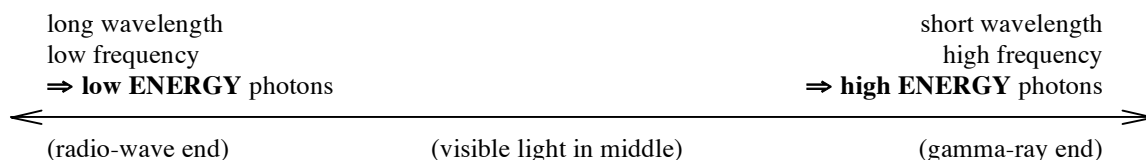

PHOTONS and PLANCK'S CONSTANT

Max Planck, in his work on explaining blackbody radiation, proposed that *energy* of electromagnetic (EM) radiation cannot have just any values (**continuous**), but is in fact **quantized**. EM radiation comes in little discrete "packets" of energy ("**photons**"), whose energy depends on the frequency of the radiation:

$$E = h f$$

energy of a photon

$h = $ **Planck's constant** $= 6.626 \times 10^{-34}$ J·s $= 4.136 \times 10^{-15}$ eV·s

The **EM spectrum** now becomes:

long wavelength   short wavelength
low frequency   high frequency
$\Rightarrow$ **low ENERGY** photons $\Rightarrow$ **high ENERGY** photons

$\longleftarrow$ ─────────────────────────────── $\longrightarrow$

(radio-wave end)   (visible light in middle)   (gamma-ray end)

PHOTOELECTRIC EFFECT

Einstein theorized (and consequently won a Nobel Prize) that if the energy of light were quantized into photons, the **photoelectric effect** would behave differently (if you varied the intensity and frequency of the light) than if light were all continuous waves. Experiment bore out the quantized hypothesis: that light behaves as discrete packets of energy. If KE_{max} = the maximum KE of electrons kicked out of the metal, $h f$ = the energy of the incoming photon, and W_0 = the "work function" of the particular metal (the minimum amount of energy to free one electron from the metal), then:

$$KE_{max} = h f - W_0 \qquad \textbf{Photoelectric Effect formula}$$

If the incoming photons have less energy than W_0, *no* electron is ejected... *no matter what the intensity* of the incoming light!

Since momentum is conserved, and since photons have been observed to collide with electrons, photons must have momentum (yes, light has momentum!):

$$p = \frac{E}{c} = \frac{h}{\lambda} \qquad \textbf{momentum of a photon}$$

WAVE-PARTICLE DUALITY of LIGHT AND MATTER

Diffraction-slit experiments show definitively that light has *wave* behavior, while photoelectric effect experiments show that light has quantized, *particle* behavior. EM waves/photons therefore possess *both* inherent characteristics: **wave-particle duality**. Each experiment exhibits more of one trait than the other. [Also, we find that high-energy EM radiation (x-rays, gamma rays) usually behave more particle-like, and low-energy EM radiation (radio waves, microwaves) usually behave more wave-like.]

If light can act like a particle, do particles of matter also behave like waves? De Broglie took this assumption and calculated the wavelength for any moving mass m at speed v, the **de Broglie wavelength**:

$$\lambda = \frac{h}{m v} \qquad \textbf{de Broglie Wavelength}$$

For most everyday objects, m is large compared to h, so their wavelengths are *undetectably* small. De Broglie wavelengths are significant only for very small masses: electrons, neutrons, etc.

ATOMIC SPECTRA

Rarefied (non-dense) gases do *not* emit a continuum of wavelengths like a blackbody; instead they emit only very specific wavelengths of light, and *only* those wavelengths. Likewise, rarefied gases don't absorb radiation at all wavelengths like blackbodies, but instead absorb only at those same specific wavelengths. When viewed through a prism or diffraction grating, the spectrum of a blackbody looks like a *continuous rainbow*, while the spectrum of a gas has *discrete* **spectral lines** only at those specific wavelengths.

Those specific wavelengths are unique to each element or molecule (like a fingerprint!), and represent wavelengths whose energies = the energy level differences between electron orbitals.

The (Bohr model) electron orbital **energy levels** for a single e^- around a single nucleus (Z = # of protons) are:

$$E_n = \frac{Z^2}{n^2} E_1 \qquad (n = 1, 2, 3, 4, \ldots) \qquad \textbf{Bohr atomic energy levels}$$

For a **hydrogen atom** specifically, the electron orbital energy levels become:

$$E_n = \frac{1}{n^2} E_1 \qquad \text{where} \quad E_1 = -13.6 \text{ eV} \qquad \textbf{ground state}$$

and we can then calculate all other energy levels:

$E_2 = -3.40$ eV   **excited states...**
$E_3 = -1.51$ eV
$E_4 = -0.85$ eV
...
$E_\infty = 0$ eV   **ionization** (the e^- is free)

When an electron undergoes **de-excitation** from an higher energy level to a lower energy level, a **photon is emitted**. The energy of this photon is: $\Delta E = E_{\text{higher}} - E_{\text{lower}} = h\,f$. When a photon of exactly one of these energy differences passes by an electron in a lower energy level, the electron may jump up to a higher energy level (**excitation**), and the **photon is absorbed**. These are collectively called electron **transitions**.

Why should electrons only be allowed to exist in these specific, discrete orbitals/energy levels, and *not* be allowed "orbit" an atom with just any amount of energy? The answer comes from the fact that the electron has wave properties (de Broglie), and it will only "orbit" an atom at those circumferences which are an *integer number of wavelengths*… i.e., those in which the electron can interfere with itself *constructively*. (At all other orbital distances, the electron wave will interfere with itself more or less *destructively*, and those "orbits" are not allowed, or *forbidden*.) Electrons may only occupy these *allowed* **orbitals**, and may jump instantaneously from one to another (excitation & de-excitation transitions), but may *not* exist in between them.

QUANTUM NUMBERS & THE PERIODIC TABLE

For a *single atom*:
n is called an electron's **principal quantum number**. n is one of 4 "quantum numbers" that describe exactly which orbital/state an electron is in:

n	principal quantum number	= energy level of electron
		= 1, 2, 3, 4, ….
l	orbital quantum number	= angular momentum of electron about nucleus
		= 0, 1, 2, …, $(n-1)$
m_l	magnetic quantum number	= component of l along one axis (important when atom is in a **B** field)
		= $-l$, …, -2, -1, 0, 1, 2, …, $+l$
m_s	spin quantum number	= "up" or "down" spin of electron
		= $+1/2$ or $-1/2$ only

These quantum numbers give rise to the structure of the periodic table. Elements with their outermost electrons in similar states (same n, or same l, for instance) have similar chemical properties:

$n \rightarrow$ rows of the periodic table
$l \rightarrow$ shape of orbitals: $s, p, d, f, …$
$m_l \rightarrow$ number of orbitals of each shape (1 s-orbital, 3 p-orbitals, 5 d-orbitals, 7 f-orbitals, etc.)
$m_s \rightarrow$ 2 electrons can occupy each of the above orbitals: one spin-up, and one spin-down.

Pauli exclusion principle: No more than 1 e^- at a time in an atom may occupy a given state (n, l, m_l, m_s).

All of the above states become *much* more complicated for *molecules*: "molecular orbitals". But once you figure out the molecular orbitals' energies, etc., the Pauli exclusion principle still applies.

QUANTUM PROBABILITY

The equations of quantum mechanics allow us to derive the shapes of atomic orbitals, etc., and predict the behavior of particles… but only **probabilistically**. We don't know *exactly* where a given e^- will be around an atom at a given moment; we can only say that it has a high probably of being close to its "orbital" shell, and a low probability of being far from it (and zero probability for a few special points in space: "nodes").

This *uncertainty* in the actual position of a particle (Δx) and the *uncertainty* in its velocity (or in this case, momentum: Δp) can never shrink to zero: **the better we know one, the worse we will know the other**. This is written mathematically as the **Heisenberg uncertainty principle**:

$$\Delta x \cdot \Delta p \geq \frac{h}{2\pi}$$ **Heisenberg's Uncertainty Principle**

This can also be written as: $\Delta E \cdot \Delta t \geq \dfrac{h}{2\pi}$ for uncertainty in Energy and time.

Wow… this means that the Newtonian idea of a **deterministic universe** (being able to use an object's position and velocity at one specific time to exactly predict both values all future times) *doesn't hold* at the atomic and subatomic level! Instead, we can only say that there is a certain *likelihood* (however large that may be) that a particle will be observed at a given location or speed at any future time. That said, we find that for most *macroscopic* objects and for *large collections* of small particles [like a mole of gas], these probabilities are all *extremely* close to 1 and 0, so that on the macroscopic level, the predictions of quantum mechanics converge to those of classical mechanics. This agreement between quantum mechanics and classical physics on macroscopic scales is called the **correspondence principle**, and is a necessary quality of a correct quantum theory.