

Lecture 3, January 23, 2006**Solved Homework**

The total power emitted by a blackbody is obtained by integrating the frequency-dependent energy density over all frequencies. Thus, we must solve

$$\rho(T) = \int_0^{\infty} \frac{8\pi h\nu^3}{c^3(e^{h\nu/kT} - 1)} d\nu$$

To solve this integral, it is most convenient to introduce a new variable $x = h\nu/kT$. In that case, we also have $dx = (h/kT)d\nu$. We may rearrange these to see what substitutions we will make in the integral for ν and $d\nu$, namely $\nu = xkT/h$ and $d\nu = (kT/h)dx$. If we introduce these substitutions we have

$$\begin{aligned}\rho(T) &= \int_0^{\infty} \frac{8\pi h \left(\frac{kTx}{h}\right)^3}{c^3(e^x - 1)} \left(\frac{kT}{h} dx\right) \\ &= \frac{8\pi k^4 T^4}{c^3 h^3} \int_0^{\infty} \frac{x^3}{(e^x - 1)} dx\end{aligned}$$

The value of the final integral can be looked up: it is $\pi^4/15$. If one plugs in all the appropriate values for the various constants, one obtains $\rho = aT^4$ where $a = 7.5657 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$. This derivation from Planck's formula agrees essentially perfectly with experiment.

The Orbiting Electron Model of the Hydrogen Atom

In the first decade of the 1900s, it began to become clear that atomic structure consisted of massive nuclei, composed of protons and neutrons, surrounded by electrons that had comparatively enormous volumes of empty space available to them. Protons and electrons attract one another through the Coulomb force (the only one of the four physical forces to really matter in Chemistry). Since atoms do not spontaneously annihilate their charged particles in fractions of a second, there must be an opposing force that repels the electrons from the nucleus. The situation just described has an obvious analogy (particularly to physicists), namely the centrifugal force of an orbiting body that opposes the gravitational force attracting it to a central mass, e.g., a planet.

The total energy of a "planetary" hydrogen atom, assuming the nucleus to be stationary, would derive from two terms: the kinetic energy of the orbiting electron and the potential energy from the Coulomb attraction. We will address each term individually.

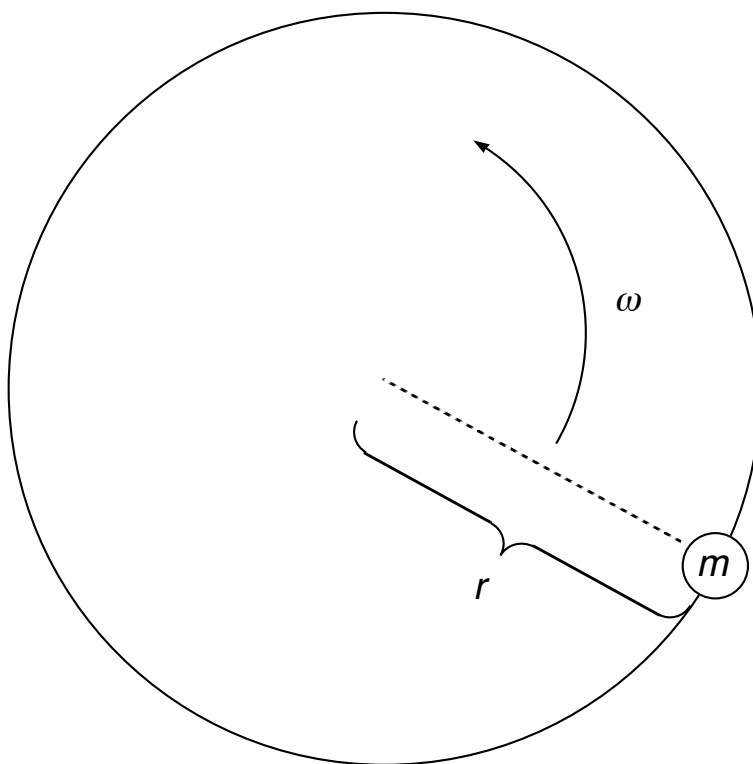
Kinetic Energy for an Orbiting Body

A convenient expression for kinetic energy, usually denoted T (not to be confused with temperature!), is

$$T = \frac{p^2}{2m} \quad (3-1)$$

where p is momentum (mass times velocity, units of mass-distance per time—it is a trivial matter to verify that this agrees with the other common expression, $T = (1/2)mv^2$).

For an orbiting body, however, it is usually more convenient not to discuss mass, velocity, and momentum, but rather the analogous quantities, moment of inertia, angular velocity, and angular momentum. To see the relationship between them easily, it is helpful to visualize the system.



The velocity at which mass m is moving is expressed in terms of distance per time. In the case of orbital motion, the particle travels around the circumference of the circle, a distance of $2\pi r$, once in each orbital frequency, ν . Angular velocity ω is defined as

$$\omega = 2\pi\nu \quad (3-2)$$

so the *total* velocity is

$$v = r\omega \quad (3-4)$$

and the kinetic energy is thus

$$T = \frac{1}{2}m(r\omega)^2 \quad (3-5)$$

To make the correspondence between linear and angular formulae more clear, one usually writes

$$\begin{aligned} T &= \frac{1}{2}(mr^2)\omega^2 \\ &= \frac{1}{2}I\omega^2 \end{aligned} \quad (3-6)$$

where I is the "moment of inertia", which is defined to be equal to mr^2 . Finally, if we recast this equation to be more in the form of eq. 3-1, we have

$$\begin{aligned} T &= \frac{(I\omega)^2}{2I} \\ &= \frac{l^2}{2I} \end{aligned} \quad (3-7)$$

where l is the angular momentum, defined to be equal to $I\omega$. It would be a good idea to always bear in mind the following relationships between linear and angular quantities *and their units* (listed in this case as SI units)

Linear quantity	Units	Angular quantity	Units
Mass, m	kg	Moment of Inertia, I	kg m ²
Velocity, v	m s ⁻¹	Angular velocity, ω	s ⁻¹
Momentum, p	kg m s ⁻¹	Angular momentum, l	kg m ² s ⁻¹

Note that the units of angular momentum are the same as those for action (recall that action is energy times time; energy has SI units of kg m² s⁻² and time is simply s). Thus, Planck's constant may be considered either to be in units of action or units of angular momentum; this will be important a bit further below.

Potential Energy of an Orbital System of Two Charged Particles

Coulomb's law states that the interaction energy between a positively charged nucleus and an electron will be

$$V = -\frac{(Ze)e}{4\pi\epsilon_0 r} \quad (3-8)$$

where Z is the atomic number (i.e., the number of protons), e is the electron charge (the charge on an electron is equal in magnitude to the charge on a proton but of opposite sign, so the nuclear charge is $-Ze$), ϵ_0 is the so-called permittivity of free space (one may regard it as a constant that makes units work out), and r is the distance between the nucleus and the electron.

The Total Energy of the Bohr Model for the Atom

If we use eqs. 3-7 and 3-8 to describe the total energy of an atom, we have

$$\begin{aligned} E &= T + V \\ &= \frac{l^2}{2I} - \frac{(Ze)e}{4\pi\epsilon_0 r} \end{aligned} \quad (3-9)$$

In order to solve for the energy, we need to know the radius of the electron's orbit, and the frequency of that orbit. That is, there are apparently two free variables. If these variables were truly to be free, we would expect the atom to be able to exist at any energy level, and emission spectra would be expected to be continuous, since transitions from any energy level to any other would be possible.

In 1913, Bohr, a Danish physicist working at the Institute for Theoretical Physics (supported by the Carlsberg brewery then and now...) proposed to eliminate one degree of freedom by insisting that the angular momentum of the electron must be quantized. In particular, he would permit l to take on only multiples of $(h/2\pi)$, i.e.,

$$\begin{aligned} l &= \frac{nh}{2\pi} \\ &= n\hbar \quad n = 1, 2, 3, \dots \end{aligned} \quad (3-10)$$

where the shorthand "h-bar" symbol \hbar is used to represent $(h/2\pi)$. Recall that h has units of angular momentum.

We may eliminate the other degree of freedom by noting that there is a relationship between r and v that is imposed by virtue of there being a stable, circular orbit. To keep the orbiting electron from flying away, there must be a force attracting it to

the nucleus. We know that force to be the Coulomb force, but we also know from classical physics that this "centripetal" force F may be expressed as

$$F = \frac{l^2}{Ir} \quad (3-11)$$

From Coulomb's law (eq. 3-8), we have that the Coulomb force is $(-dV/dr)$ or

$$F = \frac{(Ze)e}{4\pi\epsilon_0 r^2} \quad (3-12)$$

If we adopt eq. 3-10 for l and equate eqs. 3-11 and 3-12 we have

$$\frac{n^2\hbar^2}{Ir} = \frac{(Ze)e}{4\pi\epsilon_0 r^2} \quad (3-14)$$

If we now expand the moment of inertia as mr^2 and solve for r we obtain

$$r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e Z e^2} \quad (3-15)$$

where m_e is the mass of the electron. Since the quantum number n appears in eq. 3-15, the orbital radii are restricted to discrete values. The smallest radius will be for $n = 1$. If one plugs in all of the appropriate quantities for the hydrogen atom, the value of r obtained for $n = 1$ is 0.529 Å. This distance is known as the "Bohr radius", a_0 . Note that the radius would be smaller for a heavier atom (larger Z).

If we now use eqs. 3-11, 3-12, and 3-15 in eq. 3-9, we determine that the Bohr atom has discrete energy levels at

$$E_n = -\frac{m_e Z^2 e^4}{8\epsilon_0^2 \hbar^2 n^2} \quad (3-16)$$

There are many things to notice about this equation. First, the energy is always negative and bounded by zero at infinite quantum number. That is, the electron is always bound to the nucleus (positive work energy would need to be expended to strip it away). The lowest energy corresponds to $n = 1$, which is called the "ground state", and the opposite of that energy should be the ionization potential for the hydrogen atom if $Z = 1$. If we plug in all of the appropriate physical constants, we compute 13.605 eV, in essentially perfect agreement with experiment.

In addition, if we assume that the emission lines in the H atom spectrum derive from excited-state atoms emitting a photon and falling down to a lower quantum-number

state, and that the energies of those photons are equal to Planck's constant times their frequency ($E = h\nu$), then we have

$$\begin{aligned}\nu &= \frac{\Delta E_{m \rightarrow n}}{h} \\ &= \frac{m_e Z^2 e^4}{8\epsilon_0^2 h^3} \left(\frac{1}{n^2} - \frac{1}{m^2} \right)\end{aligned}\tag{3-17}$$

where $m > n$. This formula accurately predicts all lines in the H emission spectrum. Indeed, this formula was used to *predict* lines that had not yet been observed (because transitions become increasingly faint between more highly excited states) and they were then confirmed!

Wave-particle Duality

The Bohr model works extraordinarily well for one-electron atoms. It fails miserably to explain all others. Moreover, it violates a particularly key law of physics, namely that a charged particle (i.e., an electron) being accelerated in an electric field (i.e., the centripetal acceleration and the electric field created by the nucleus) will give off energy in the form of radiation. That is, the electron should spiral into the nucleus and die.

One way to avoid this problem would be to imagine that the electron is not a particle. Of course, it comes in integral quantities, and experiments reveal tracks and localized interactions between electrons and surrounding media. In this regard, however, it is no different than light. Light shows many wavelike properties (destructive interference in the double-slit experiment, for example) but it also shows particle-like properties (the photoelectric effect, discussed last lecture, for example).

In his theorems of relativity, Einstein had shown that the total energy of a system was equal to its mass times the speed of light squared, i.e.,

$$E = mc^2\tag{3-18}$$

where c is the speed of light. We also have from the Bohr postulate, for a photon,

$$E = h\nu\tag{3-19}$$

For light, we have the relation

$$c = \lambda\nu\tag{3-20}$$

so we may combine the above 3 formulae to determine the photon's momentum, mc , which is given by

$$p = \frac{h}{\lambda} \quad (3-21)$$

In 1924, de Broglie, who was a physicist working in Paris (he began as a history major, but duty in radio communications during WWI sparked his interest in science), reasoned that eq. 3-21 would be obeyed by *any* particle possessing momentum. The de Broglie wavelength is thus defined as

$$\lambda = \frac{h}{p} \quad (3-22)$$

Experimental confirmation of matter behaving as waves arrived in 1927 when Bell Labs demonstrated that a beam of electrons showed a diffraction pattern when bounced off a nickel surface—de Broglie was awarded the Nobel prize in Physics in 1929 for his work.

A key feature of de Broglie's insight is that it provides a foundation for the Bohr quantization hypothesis. If we regard the orbiting electron in the Bohr atom not as a particle, but as a standing wave, then the circumference of the orbit ($2\pi r$) must be an integral number of wavelengths (otherwise the wave will destroy itself through destructive interference as it continually propagates). This, then, establishes a different restriction on r and v . We have

$$n\lambda = 2\pi r \quad n = 1, 2, 3, \dots \quad (3-23)$$

Substituting in eq. 3-22 for λ gives

$$\frac{nh}{p} = 2\pi r \quad (3-24)$$

which can be trivially rearranged to eq. 3-10, the Bohr hypothesis.

Note, incidentally, that you and I do *not* diffract as we wander through the world. That is because we have fantastically tiny de Broglie wavelengths when we are moving (on the order of 10^{-35} m...) However, as masses become small enough, wavelengths become larger.

Have you noticed that eq. 3-22 makes the rather odd prediction that a particle at rest (zero momentum) has an infinite wavelength? This is somewhat analogous to the quantum mechanical uncertainty principle, which we will address later on.

Homework

To be solved in class:

What accelerating voltage is needed to give an electron a de Broglie wavelength of 0.1 nm?

To be turned in for possible grading Jan. 27:

For Li^{2+} , what is the longest wavelength that can be emitted by an electron ending in the $n = 3$ state?