

Lecture 2, January 20, 2006

**The state of Physics and Chemistry at the turn of the 20th Century**

To appreciate quantum mechanics, it is important to have some feel for the state of science, and in particular physics, in the years around 1900. Two key points should be made:

- 1) Many physicists felt that all of the key laws describing the manner in which the Universe worked had essentially been discovered. Dirac (about whom we will learn more later in the course) when looking for a field of study was advised by a senior physicist to avoid physics because "there is nothing important left to discover". The feeling was that all that was left was the polishing of a few details.
- 2) The bridge between physics and chemistry was beginning to be made solid. The enormous contributions of Gibbs in the United States and Boltzmann in Austria had forged links between chemistry and classical and statistical thermodynamics, respectively (these last two being primarily fields of physics at the time). The power of thermodynamic formulae to rationalize the behavior of gases, liquids, and solids had a tremendous impact on chemistry, which up to that point had tended to be a science in which rules were discovered empirically, without too much concern for explaining the physical foundation of those rules. In part, this derived from European politics, as Chemistry was fractured along nationalistic lines, with the Germans dominating organic chemistry, the English and Swedes dominating physical chemistry, and the French excelling in analytical and inorganic chemistry. After a long debate over the existence of atoms,\* the matter was beginning to be considered settled.

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\* Ernst Mach (for whom the unit of speed is named) was a member of the Faculty of Philosophy at Vienna during this time, this being the same school where Boltzmann was the Head of Physics. The two engaged in many acrimonious debates about the existence of atoms, and about the utility of equations to represent physical laws. Mach held, as a *philosophy*, that nothing was real that could not be directly observed by an individual using only human senses—atoms being too small to be seen, any belief in their existence was simply faith, and not science. Mach also maintained that there were no physical laws, and that the suggestion that two events could be related as cause and effect was illegitimate. All one could do would be to note that, up until now, the effect always seemed to follow the cause, but going any further would not be justified. Mach especially objected to interpreting equations that successfully described some chemical or physical phenomenon so as to make predictions about the nature of the species involved (e.g., atoms or molecules)!

Into this relative complacency, the philosophical bomb of quantum mechanics was introduced with a slow burning fuse.

### What is Quantization?

To say that something is quantized is to imply (i) that it is quantifiable and (ii) that it can only take on a certain number (albeit possibly infinite) of discrete values. For example, populations of living creatures are quantized. In this case, the discrete values are whole numbers (fractional creatures tending not to be alive...) Indeed, most populations of things—where we have a definition that says something either "is" or "is not" the thing in question—are quantized to whole numbers.

Quantization need not be limited to whole numbers, however. For example, the prices of stocks on the New York Stock Exchange are quantized in units of \$0.01 (until a few years ago they were quantized to certain fractions of a dollar other than  $n/100$ ).

By contrast, there are many things that are *not* quantized, which is to say that they are quantifiable, but that they can take on *any* of a continuous range of values within some infinite interval. The volume of beer in a pint glass, for example, is not quantized; it can take on any value between empty (zero) and full (one pint); the experimental test of this prediction is a favorite pastime of chemists and physicists alike...

Most physical quantities in *classical* physics are *not* quantized. For example, mass can take on any value. Velocity can take on any value. Energy (which can be converted to work or heat) can take on any value. If we consider some of the classical equations of physics, e.g.,

$$F = m \cdot a \quad (2-1)$$

where  $F$  is force,  $m$  is mass, and  $a$  is acceleration and

$$W = F \cdot d \quad (2-2)$$

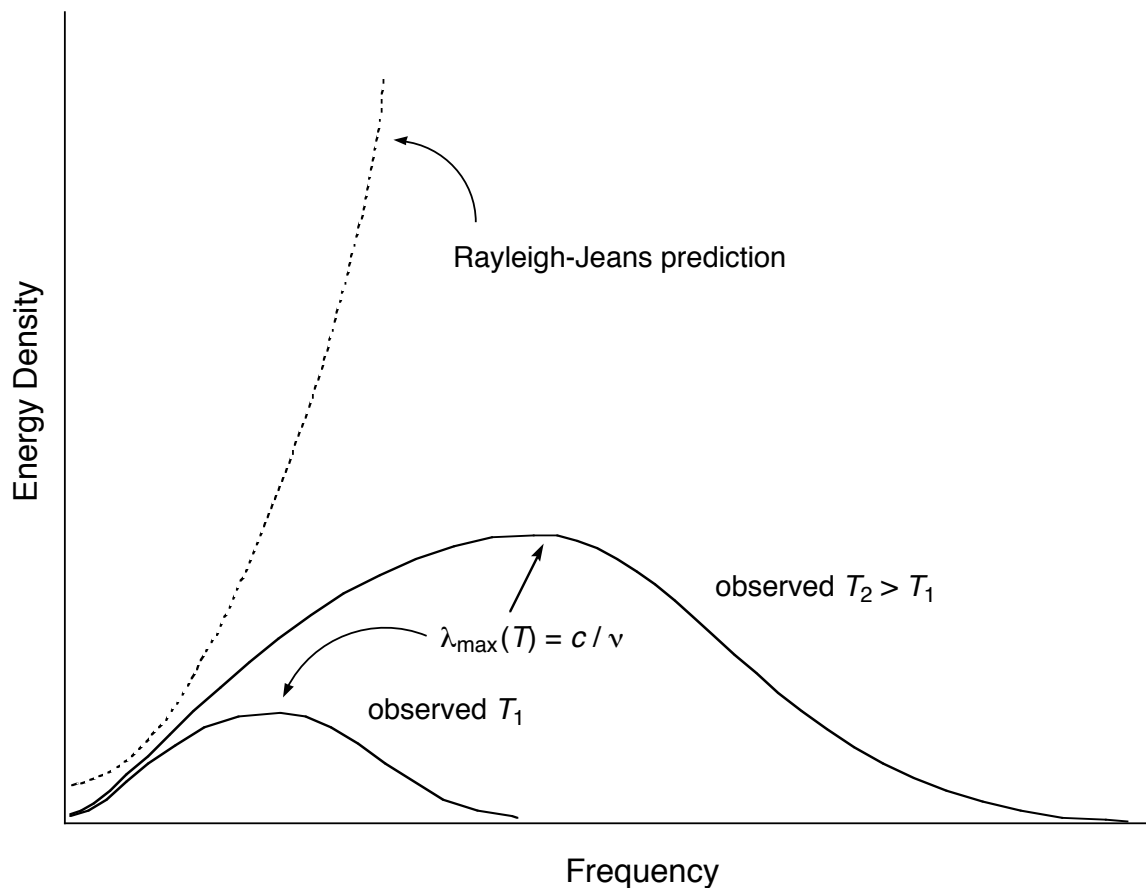
where  $W$  is work and  $d$  is distance, it seems clear that there should be no restriction on the values that these quantities can take on.

### The First Quantum Assumptions

*Blackbody Radiation.* A blackbody is an object that perfectly re-emits radiation incident upon it without any *reflection* of that radiation. Although the incident radiation can be of arbitrary wavelength, a blackbody is empirically observed to radiate a spectrum of wavelengths having a characteristic energy density at each frequency. Classical physics predicts (we won't derive this) that the relationship between the energy density and the frequency of the radiation is

$$\rho(\nu, T) = \frac{8\pi kT}{c^3} \nu^2 \quad (2-3)$$

where  $\rho$  is the energy density in units of energy per volume (e.g.,  $\text{J}\cdot\text{m}^{-3}$ ),  $\nu$  is the frequency of *emitted* radiation,  $T$  is the temperature of the blackbody (resulting from absorption of the incident radiation),  $k$  is Boltzmann's constant, and  $c$  is the speed of light. This is known as the Rayleigh-Jeans law. A clear implication of the Rayleigh-Jeans law is that as the frequency becomes larger, the energy density increases as the square of the frequency. This is known as the "ultraviolet catastrophe", since it is well known that blackbody emitters like stars, for example, have clear maxima in their emission spectra.



Max Planck, a German physicist in Berlin, attempted to resolve this problem. He started from a fairly standard assumption, namely that a blackbody could be modeled as a collection of oscillators, each one of which can absorb or emit radiation. However, he then made a radical assumption. He insisted that the oscillators could only take on discrete, quantized energies, these energies being described as

$$\varepsilon_n = nh\nu \quad (2-4)$$

where  $\varepsilon$  is the oscillator energy,  $n$  is a whole number (0, 1, 2, ...),  $\nu$  is the frequency, and  $h$  is some arbitrary constant having units of action (energy-time, since frequency is in units of time<sup>-1</sup>). Within the context of this assumption, and using various laws of thermodynamics, Planck derived an alternative to the Rayleigh-Jeans formula, namely

$$\rho(\nu, T) = \frac{8\pi h \nu^3}{c^3 (e^{h\nu/kT} - 1)} \quad (2-5)$$

Note that eq. 2-5 has proper behavior at high frequencies (the exponential dominates the cubic in  $\nu$  and  $\rho$  goes to zero). Note also that we can use the series expansion for the exponential

$$e^{h\nu/kT} = 1 + \frac{h\nu}{kT} + \frac{1}{2!} \left( \frac{h\nu}{kT} \right)^2 + \dots \quad (2-6)$$

to see that at low frequencies, where we may truncate eq. 2-6 after the first term in  $\nu$  without much loss of accuracy, we recover the Rayleigh-Jeans formula. This is as it should be since very small  $\nu$  makes the energy spectrum of each oscillator effectively continuous (see eq. 2-4). Invoking quantization is required, then, for correct behavior at *high* frequencies.

The constant  $h$  has come to be called Planck's constant, and its value is  $6.626 \times 10^{-34}$  J-s. In 1918, Planck won the Nobel prize in physics for his efforts. His success was balanced by many personal tragedies. He and his wife lost two daughters in childbirth, a son in combat in WWI, and another son was executed as a participant in the plot to assassinate Hitler in 1944. Planck served as a reluctant pawn of the Nazis for many years, running the Kaiser-Wilhelm Institute in Berlin (the best research University in Germany) in the hopes of protecting its workers from the tyranny of Nazi science.

*The Photoelectric Effect.* When metals are bombarded with incident light (radiation), electrons can be ejected from them. However, there is a threshold frequency below which, no matter how intense the light beam used, no electrons are ejected. This violates *classical* rules of physics, since the total energy contained in a brilliant beam of somewhat lower frequency is much greater than the total energy in a dim beam of higher frequency.

More interestingly, the kinetic energy of the ejected electrons for a given frequency of light that *does* eject them is observed to be a constant that depends only on the light frequency, *not* its intensity. A brighter beam knocks out more electrons, but they all have the same kinetic energy. Einstein in 1905, being aware of the work of Planck, also made use of a quantum hypothesis to explain this effect. He posited that each electron was ejected by the impact of a *particle* of light (a "photon"), and that the relationship between the frequency of the photon and the electron kinetic energy was

$$h\nu = \frac{1}{2}m_e v^2 + \phi_{\text{metal}} \quad (2-7)$$

where  $h$  is Planck's constant,  $\nu$  is the photon frequency,  $m_e$  is the mass of an electron,  $v$  is the electron velocity (i.e., the first term on the right-hand side is the electron kinetic energy; be careful in physical equations not to confuse Greek nu “ $\nu$ ” and Roman “ $v$ ”!), and  $\phi$  is the "work function" that is a characteristic of the particular metal (it can be thought of as how “tightly” the metal holds its electrons). In the absence of  $h\nu$  exceeding the work function, no electrons are ejected.

Einstein won the Nobel prize for this work. He did *not* win the Nobel for relativity, as many people assume. Physicists hated relativity for years, particularly those in the Swedish Royal Academy (which selects laureates), and this prejudice prevented Einstein from receiving additional recognition for this other earthshaking discovery.

*Heat Capacity of Perfect Crystals.* Classical thermodynamics states that the molar heat capacity of a perfect crystal is  $3R$  where  $R$  is the universal gas constant (the law of Dulong and Petit). Alas, at low temperatures, experiment clearly shows that the molar heat capacity goes to zero. So much for the beautiful theory of *classical* thermodynamics...

Einstein in 1907 (he was a busy fellow in those years) proposed that the vibrations of the atoms in the crystal (the phenomenon that is responsible for its heat capacity) are *quantized* by the same formula as eq. 2-4, except that now  $\nu$  is not a light frequency, but a mechanical vibrational frequency. With this assumption, Einstein obtained excellent agreement with experiment for heat capacities at low temperatures. At about this point, people began to take serious notice of quantization. (Ironically, Planck was one of those longest to resist the legitimacy of quantization, even though he had introduced the idea. He remained convinced for many years that another derivation would be found that would remove the need for quantization in the various phenomena presented thus far, but eventually he became a true believer as well.)

*Hydrogen Emission Spectrum.* When atomic hydrogen (which can be made at very low pressure) is either heated or subjected to large electrical discharges, it emits light. However, it emits only at certain very specific frequencies, rather than as a broad spectrum. Careful analysis of the lines reveals that they occur at frequencies that can be predicted from the equation

$$\nu = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (2-8)$$

where  $R$  is the Rydberg constant  $109677.8 \text{ cm}^{-1}$  (*not* the universal gas constant! there are only so many letters, unfortunately...) and  $n_1$  and  $n_2$  are whole numbers with the former smaller than the latter. At the time of this observation, no one had a good explanation for

*why* the so-called Balmer-Rydberg-Ritz formula eq. 2-8 worked, but the appearance of quantum numbers within it was certainly provocative.

### **Homework**

To be solved in class:

Given the validity of eq. 2-5, what is the total power emitted from a blackbody radiator at temperature  $T$ ? That is, what is the sum of the energy density integrated over all possible frequencies? You will likely need to resort to an integral table in order to solve this problem. If you've never used one before, they're easy to find on the web, in addition to sources like the CRC Handbook of Chemistry and Physics.

To be turned in for possible grading Jan. 27:

What is the maximum number of electrons that can be emitted if a potassium surface of work function 2.40 eV absorbs  $3.25 \times 10^{-3}$  J of radiation at a wavelength of 300 nm? What is the kinetic energy and velocity of the emitted electrons?