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## **Transition Probabilities**

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When he finished the years needed to complete his general theory of relativity, Einstein turned back to quantum theory and to Bohr's two postulates about 1) electrons in stationary (non-radiating) states and 2) radiating energy  $E_m - E_n = hv$  when "jumping" (Einstein's word from 1907) between two energy levels.

Relativity

Bohr's two postulates provided amazingly accurate explanations of the spectroscopic lines in the hydrogen spectrum. They became the basis for a theory of atomic structure that is still taught today as the introduction to quantum chemistry.

But Bohr, and Planck, *used* expressions that cleverly fit known spectroscopic data. In 1916, Einstein showed how to *derive* Bohr's second postulate from more fundamental physical *principles*, along with Einstein's latest, and thus far simplest, *derivation* of the Planck radiation law that demonstrated its discrete nature.

Where Bohr and Planck manipulated mathematical expressions to make them fit experimental data, Einstein derived the *transition probabilities* for absorption and emission of light quanta when an electron jumps between Bohr's energy levels. Starting with "Boltzmann's Principle" that defines entropy *S* as probability, calculated as the number of possible states *W*, and using fundamental conservation laws for energy and momenta, Einstein showed his deep physical understanding of interactions between electrons and radiation that went back over ten years., but had not been accepted by his colleagues, not even Planck or Bohr.

Planck had speculated for many years that the *irreversibility* of the entropy increase somehow depends on the interaction of radiation and matter. Now Einstein's expressions for the absorption and emission of light quanta showed how they maintain thermodynamical equilibrium between radiation and matter as well as how some interactions are indeed *irreversible*.

In addition, Einstein predicted the existence of the unidirectional "stimulated emission" of radiation, the basis for today's lasers.

Most amazingly, Einstein showed that quantum theory implies the existence of ontological *chance* in the universe.

At this time, Einstein felt very much alone in believing the reality (his emphasis) of light quanta:

I do not doubt anymore the *reality* of radiation quanta, although I still stand quite alone in this conviction.<sup>1</sup>

In two papers, "Emission and Absorption of Radiation in Quantum Theory," and "On the Quantum Theory of Radiation," he again derived the Planck law. For Planck it had been a "lucky guess" at the formula needed to fit spectroscopic measurements.

Einstein derived "transition probabilities" for quantum jumps, describing them as A and B coefficients for the processes of absorption, spontaneous emission, and (his newly predicted) stimulated emission of radiation.

In these papers, Einstein *derived* what had been only a postulate for Planck' (E = hv). He also derived Bohr's second postulate  $E_m - E_n = hv$ . Einstein did this by exploiting the obvious relationship between the Maxwell-Boltzmann distribution of gas particle velocities and the distribution of radiation in Planck's law.<sup>2</sup>

The formal similarity between the curve of the chromatic distribution of thermal radiation and the Maxwellian distribution law of velocities is so striking that it could not have been hidden for long. As a matter of fact, W. Wien was already led by this similarity to a farther-reaching determination of his radiation formula in his theoretically important paper, where he derives his displacement law... Recently I was able to find a derivation of Planck's radiation formula which I based upon the fundamental postulate of quantum theory, and which is also related to the original considerations of Wien such that the relation between Maxwell's curve and the chromatic distribution curve comes to the fore. This derivation deserves attention not only because of its simplicity, but especially because it seems to clarify somewhat the still unclear processes of emission and absorption of radiation by matter. I made a few hypotheses about the emission and absorption of radiation by molecules,

<sup>1</sup> Letter to Besso, in Pais, 1982, p.411

<sup>2</sup> See Figure 4-3. "Distribution laws for radiation and matter" on page 33

which suggested themselves from a quantum-theoretic point of view, and thus was able to show that molecules under quantum theoretically distributed states at temperature equilibrium are in dynamical equilibrium with Planck's radiation. By this procedure, Planck's formula followed in an amazingly simple and general manner. It resulted from the condition that the distribution of molecules over their states of the inner energy, which quantum theory demands, must be the sole result of absorption and emission of radiation. If the hypotheses which I introduced about the interaction between radiation and matter are correct, they must provide more than merely the correct statistical distribution of the inner energy of the molecules. Because, during absorption and emission of radiation there occurs also a transfer of momentum upon the molecules. This transfer effects a certain distribution of velocities of the molecules, by way of the mere interaction between radiation and the molecules. This distribution must be identical to the one which results from the mutual collision of the molecules, i.e., it must be identical with the Maxwell distribution...

When a molecule absorbs or emits the energy *e* in the form of radiation during the transition between quantum theoretically possible states, then this elementary process can be viewed either as a completely or partially directed one in space, or also as a symmetrical (nondirected) one. *It turns out that we arrive at a theory that is free of contradictions, only if we interpret those elementary processes as completely directed processes.*<sup>3</sup>

If light quanta are particles with energy E = hv traveling at the velocity of light c, then they should have a momentum p = E/c = hv/c. When light is absorbed by material particles, this momentum will clearly be transferred to the particle. But when light is emitted by an atom or molecule, a problem appears.

If a beam of radiation effects the targeted molecule to either accept or reject the quantity of energy hv in the form of radiation by an elementary process (induced radiation process), then there is always a transfer of momentum hv/cto the molecule, specifically in the direction of propagation of the beam when energy is absorbed by the molecule, in the opposite direction if the molecule releases the energy. If the

<sup>3</sup> CPAE, vol.6, Doc. 38, "On the Quantum Theory of Radiation,", p.220-221.

molecule is exposed to the action of several directed beams of radiation, then always only one of them takes part in an induced elementary process; only this beam alone determines the direction of the momentum that is transferred to this molecule. If the molecule suffers a loss of energy in the amount of hv without external stimulation, i.e., by emitting the energy in the form of radiation (spontaneous emission), then this process too is a directional one. There is no emission of radiation in the form of spherical waves. The molecule suffers a recoil in the amount of hv/c during this elementary process of emission of radiation; the direction of the recoil is, at the present state of theory, determined by "chance." The properties of the elementary processes that are demanded by [Planck's] equation let the establishment of a quantumlike theory of radiation appear as almost unavoidable. The weakness of the theory is, on the one hand, that it does not bring us closer to a link-up with the undulation theory; on the other hand, it also leaves time of occurrence and direction of the elementary processes a matter of "chance." Nevertheless, I fully trust in the reliability of the road taken.<sup>4</sup>

Conservation of momentum requires that the momentum of the emitted particle will cause an atom to recoil with momentum hv/c in the opposite direction. However, the standard theory of spontaneous emission of radiation is that it produces a spherical wave going out in all directions. A spherically symmetric wave has no preferred direction. In which direction does the atom recoil?, Einstein asked:

An outgoing light particle must impart momentum hv/c to the atom or molecule, but the direction of the momentum can not be predicted! Neither can the theory predict the time when the light quantum will be emitted. Einstein called this "weakness in the theory" by its German name - *Zufall* (chance), and he put it in scare quotes. It is only a weakness for Einstein, of course, because his God does not play dice.

Such a random time was not unknown to physics. When ERNEST RUTHERFORD derived the law for radioactive decay of unstable

<sup>4</sup> CPAE, vol.6, Doc.38, "On the Quantum Theory of Radiation,", p.232.

atomic nuclei in 1900, he could only give the probability of decay time. Einstein saw the connection with radiation emission:

It speaks in favor of the theory that the statistical law assumed for [spontaneous] emission is nothing but the Rutherford law of radioactive decay.  $^5$ 

Einstein clearly saw that the element of chance that he discovered threatens *causality*. It introduces *indeterminism* into physics.

The indeterminism involved in quantizing matter and energy was known, if largely ignored, for another decade until WERNER HEISENBERG's quantum theory introduced his famous *uncertainty* (or *indeterminacy*) principle in 1927, which he said was *acausal*.

Where Einstein's indeterminism is qualitative, Heisenberg's principle is quantitative, stating that the exact position and momentum of an atomic particle can only be known within certain (*sic*) limits. The product of the position error and the momentum error is greater than or equal to Planck's constant  $h/2\pi$ .

 $\Delta p \Delta x \ge h/2\pi.$ 

See chapter 21.

Irreversibility

We shall see in the next chapter that the interaction of the light quantum with matter, especially the transfer of momentum hv/c in a random direction, introduces precisely the element of "molecular chaos" that LUDWIG BOLTZMANN speculated might exist at the level of gas particles.

Planck had always thought that the mechanism of irreversibility would be found in the interaction of radiation and matter. Planck's intuition was correct, but in the end he did not like at all the reasons why his *microscopic* quantum would be the thing that produces the *macroscopic* irreversibility of the second law of thermodynamics.

And Planck's hopes for the second law becoming an *absolute* principle were dashed when Einstein showed that the quantum world is a *statistical* and *indeterministic* world, where ontological chance plays an irreducible foundational role.

<sup>5</sup> CPAE vol.6,Doc.34, p.216