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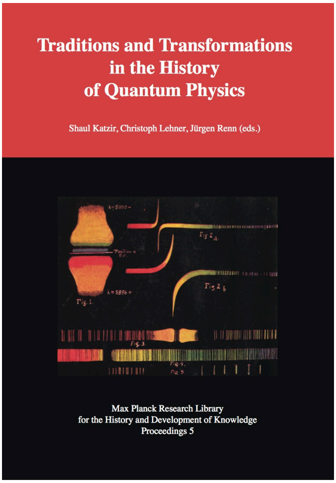
# The Origins of Maria Göppert's Dissertation on Two-Photon Quantum Transitions at Göttingen's Institutes of Physics 1920-1933



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# Chapter 8
# The Origins of Maria Göppert's Dissertation on Two-Photon Quantum Transitions at Göttingen's Institutes of Physics 1920-1933
*Barry R. Masters*

In the 1920s, the University of Göttingen was a nexus of theoretical and experimental physics, as well as mathematics (Hund 1983; 1987; Jungnickel and McCormmach 1986; Rupke 2002). In this case study of Maria Göppert, a doctoral student under the tutelage of the theoretical physicist Max Born, we see the influence of the experimental groups in James Franck's physics institute and the role of Paul Dirac's scientific papers on her dissertation research (Kamp et al. 1983).

Göppert's dissertation work on the theory of two-photon[1] transitions of atoms is significant in the history of quantum mechanics. It not only provided a theoretical foundation for the experimental findings that were the origin of her research, but more importantly, it served as the basis of nonlinear optics (Boyd 2008; Masters and So 2004).

This paper seeks to answer the following historical questions. Why did Göppert choose to study at the University of Göttingen? How did she become a student of Born? What influenced her selection of a research problem for her dissertation work? What theoretical techniques did she use in her research? And finally, why did Göppert, and not others, calculate the probability for two-photon transitions?[2]

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[1] Göppert wrote "two light quanta" (*zwei Lichtquanten*) in her publications. In 1926, Gilbert N. Lewis coined the term "photon." The modern usage is "two-photon" or "multi-photon" processes (Masters and So 2008).

[2] Göppert's theory predicted two-photon absorption and emission processes of atoms in her 1931 Göttingen dissertation. Since double or two-photon transitions are related to the square of the intensity of light, they are extremely improbable with the light sources available prior to the development of the laser (Maiman 1960). In honor of her important discovery, the two-photon absorption cross-section unit, GM, is given the name Göppert-Mayer.

This paper examines the sources and reconstructs Göppert's 1931 Göttingen dissertation to answer these questions and improve our understanding of the history of quantum mechanics.[3]

In addition, the methods used in my research include an analysis of the following sources: Dirac's 1927 paper on the emission and absorption of radiation written during his visit to Bohr in Copenhagen, and Dirac's 1927 dispersion paper that he wrote in Göttingen while he was a visitor in Born's Institute of Theoretical Physics.[4]

Other sources include experimental studies described in the 1928 papers of Otto Oldenberg and those of Franck from Göttingen's physics institute, and Göppert's 1929 paper and her 1931 Göttingen dissertation, as well as her contributed chapter on dispersion theory for Born and Pascual Jordan's *Elementare Quantenmechanik* (M. Born and Jordan 1930). Part of my methodology was a comparison of all of these sources and an analysis of which theoretical techniques Göppert took from Dirac's publications and which were her original contributions.

The case study of Göppert's dissertation illustrates the synergistic interaction between Franck's experimental group and Born's theoretical group at the Göttingen physics institutes in the 1920s. Furthermore, this paper examines the role of visitors to the physics institutes. In particular, I compare the influence of Dirac on two of Born's contemporary doctoral students: Göppert, the focus of this paper, and Victor Weisskopf. I posit that the combination of her mathematical expertise, physical insight, and the selection of a research topic associated with two-photon processes, together with a deep understanding of the theoretical techniques used in Dirac's dispersion paper, all contributed to Göppert's successful theoretical prediction and calculation of the probabilities of two-photon processes.

## 8.1 Physics in Germany at the Beginning of the Twentieth Century and the Development of the Institutes of Physics at the University of Göttingen

Theoretical physics began a strong tradition in Göttingen, beginning with Woldemar Voigt. In 1883, Voigt became a full professor for theoretical (mathematical)

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[3] I use her maiden name, Göppert, as she did prior to 1931. The authorship of her 28 October 1929 paper in *Die Naturwissenschaften* is listed as Göppert. On 18 January 1930, she married Joseph Mayer, an American Rockefeller Fellow who was an assistant to James Franck. In March, she completed her final examination and the Göttingen dissertation. Afterwards, she signed her Göttingen dissertation of 7 December 1930, which was published in *Annalen der Physik* (Leipzig) in 1931, with the name Göppert-Mayer. After 1931, I refer to her married name as she did in her publications.

[4] Dirac visited Bohr in Copenhagen from September 1926 through February 1927, when he wrote his paper on transformation theory as well as his paper on the emission and the absorption of radiation by matter (Dirac 1927a; 1927b). Following that visit to Bohr, Dirac remained in Göttingen from February through the end of June 1927 (Bacciagaluppi and Valentini 2009, 84; Kragh 1990, 43). During this time he wrote his paper on dispersion theory (Dirac 1927c).

physics, as well as the director of the mathematical physics institute; in addition, he was made the co-director of the physical department of the mathematical-physical seminar (Jungnickel and McCormmach 1986, 115; Hund 1987, 30).

At the beginning of the twentieth century, many physics departments in German universities were dedicated to experimental work, however, there were also institutes of theoretical physics and full (ordinary) professors of theoretical physics (Eckert 2001; Heilbron 1967; Hund 1987; Jungnickel and McCormmach 1986; Rupke 2002; Seth 2010). In 1914, Peter Debye joined the university and became director of the institute for theoretical physics.[5]

Debye's lectures, during 1917–1918 for example, included the following topics: new research in quantum theory, optics for physicists and mathematicians. Also, Debye and David Hilbert initiated the joint seminar "On the Structure of Matter" (Schirrmacher 2003).

When Debye left Göttingen in 1920, his replacement was the theoretician, Born. Prior to his departure, Debye collaborated with Hilbert, and with the arrival of Born in Göttingen, he was offered the directorship of the mathematical department of the physics institute, formerly held by Debye. But Born exploited the confusion of the postwar ministry of culture and convinced them to divide Debye's former department into two new departments, one for theory and another for experimental research (Hund 1987; Jungnickel and McCormmach 1986, 357). Born arranged for his friend Franck, an experimentalist, to become an ordinary professor in the adjacent institute. Franck's research was centered on experimental atomic physics.

Shortly after, in 1921, three institutes were created: Robert Pohl directed the First Institute of Physics, Franck directed the Second Institute of Physics, and Born directed the Institute for Theoretical Physics. Pohl, who was made an ordinary professor of physics in 1920, was one of the founders of experimental solid state physics (Hund 1987; Jungnickel and McCormmach 1986).[6]

The scientific collaboration between Born and Franck extended beyond friendship; it was bilaterally synergistic. Born and Franck were friends and colleagues who closely interacted, and their physics institutes were located in the same building (Hund 1983; 1987).[7]

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[5] As described by Jungnickel and McCormmach (1986, 301), after Hilbert heard Debye's lecture, he decided to have Debye join the faculty in Göttingen. In order to have Debye head an institute, Voigt agreed to turn the directorship of the institute over to Debye with the agreement that Voigt would still share the institute and the teaching of theoretical physics.

[6] These institutes were in the main physics building on Bunsenstrasse, which was built in 1905. The Mathematics Institute was next door to the Physics Institutes. Ludwig Prandtl headed the Institute for aerodynamics research that was on the opposite side of Bunsenstrasse (Hentschel 1999; Hund 1987).

[7] The life-long friendship between Born and Franck began when they were both students at the University of Heidelberg and met in a mathematics class (Greenspan 2005, 24–25; Lemmerich 2007, 24).

The productive synergism between Born and Franck's groups is further described in a recent biography of Franck (Lemmerich 2007), and is expressed by Gyeong-Soon Im:

> After Born moved from Frankfurt to Göttingen in 1921, he conducted a research program in quantum theory with a distinct style: he selected as simple physical problems as possible for which there already existed extensive empirical evidence. He then sought general solutions to these problems with the help of rigorous mathematical techniques. Since Franck systematically performed experiments associated with the quantum theory, he accumulated *inter alia* many observational results on quantum excitation during collision processes, including ionization energies of atoms and molecules. Born's close collaboration with Franck was well suited to his research style: a formal and mathematical description of nature based upon plentiful observational data. (Im 1995, 74)

## 8.2 Göppert as a University and Doctoral Student

What influences impact the development of a scientist? Is it family, friends, neighbors, teachers and mentors? Is it primary education and university education? In Göppert's scholarly development, we can trace multiple examples of these influences (Johnson 1999; 2004; Masters 2000; 2008a; McGrayne 1993).

Göppert was born in 1906, the only child of Friedrich Göppert and his wife, Maria. In 1910, the family moved to Göttingen, where Friedrich Göppert obtained a position as professor. Göppert was proximate to this center of intellectual activity and her family was physically and socially connected to many of Göttingen's great intellectuals. For example, the Göpperts lived next door to Hilbert and they were personal friends. In 1921, Göttingen brought two new physicists to the university, first Born and then Franck (H. Born and M. Born 1962). The Göpperts became and remained their good friends. Other family friends included Richard Courant, Edmund Landau, and Hermann Weyl, who were members of the mathematics faculty. Göppert's own close friends included Born, Max Delbrück, Franck, Linus Pauling, Hertha Sponer, Leo Szilard, and Victor Weisskopf (McGrayne 1993; Sachs 1982).

In this section, I explore some of the plausible reasons why the young Göppert chose to study and then to perform her doctoral research in Göttingen, and after she earned her doctorate, why she chose to fulfill her professional life as a physicist outside of Germany.

There are three reasons why Göppert chose to study at Göttingen. First, Göppert fostered a strong interest in mathematics. Göttingen was home to

Germany's leading mathematics department (Jungnickel and McCormmach 1986; McGrayne 1993; Rowe 1989). Another important attraction for her was that Hilbert, Richard Courant and Carl Runge were interested in both physics and mathematical physics, which coincided with her joint interests (Hund 1987; Schirrmacher 2003).[8]

Second, Göttingen and its university had a long and famous standing in liberalism and freedom from censorship (Georg-August Universität 2011a; 2011b).[9]

Third, the University of Göttingen was home to some outstanding women, and that set a precedent and provided role models for Göppert to pursue her graduate work at that institution. For example, Emmy Noether came to Göttingen in 1916 at the invitation of both Hilbert and Felix Klein, remaining there until 1934. It was the efforts of Hilbert, a strong proponent of women's educational rights, that helped Noether undergo her habilitation[10] and thus gave her the right to lecture at a university. Finally in 1922, with a doctorate earned thirteen years previously, Noether was made a *Privatdozent*; now she could legally teach in the university under her own name. In the course of her second habilitation lecture, she presented her work on invariant forms in mathematics, or what is now known as "Noether's Theorem." In 1922, she did not receive the status of a civil servant (*Beamtin*) and she had the following title: *nichtbeamteter außerordentlicher Professor*. This was basically a volunteer professorship that had no university salary, although she received student's fees as a *Privatdozent*; in Göttingen she was never made a full professor (McGrayne 1993, 175–200).

Hertha Sponer, who was a friend of Göppert's, worked on molecular spectroscopy and photochemistry in Franck's laboratory during the time that Göppert was a graduate student with Born (Lemmerich 2007). Sponer had studied at the University of Tübingen, but after one year in Tübingen she moved to the University of Göttingen where she was a doctoral student with her supervisor, Debye. She graduated in 1921 with a doctorate; this was a very significant achievement since she was part of a small group of women who obtained a doctorate in physics at a German university in addition to her habilitation (obtained under Franck's supervision in 1925).

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[8] When Born studied for both his doctorate and his habilitation in Göttingen, he was influenced by famous scientists and mathematicians including Klein, Hilbert, Hermann Minkowski, Runge, Karl Schwarzschild (full professor of astronomy and director of the observatory), and Voigt.

[9] Consistent with this liberal spirit is the story of the Göttingen Seven (Lampe 2002; Marchand 1996). In 1837, Dahlmann and the other six protesters demonstrated against any alteration of the constitution of the Kingdom of Hanover. They were all dismissed from the university.

[10] In Germany and other European countries, before a person with a research doctorate could teach in the university, they had to obtain a habilitation which gave them this right. Habilitation research differs from the research doctorate; while the research doctorate is performed under the supervision of a guiding professor, habilitation research is based on independent scholarly work. In general, the level of scholarship for the habilitation is significantly higher as compared to the research doctorate.

Göppert's first plan was to study mathematics, which was her strongest interest. Therefore, in 1924 Göppert began her studies in mathematics at the University of Göttingen. Shortly after beginning her studies, Born asked her to join the physics seminar, and her interest in the newly-evolving area of quantum mechanics—coupled with her training and interest in mathematics—influenced her move from mathematics to physics (Greenspan 2005). By the time she became a graduate student under Born, she was already adept in mathematics and that helped her with the new quantum mechanics. Nevertheless, Franck's strong experimental approach remained with her during her doctoral research, as well as in her later works in the field of nuclear physics (Masters 2000, 38–41).

Göppert worked in Born's institute from 1924 until she graduated in 1931. After a period in the United States, she returned to Göttingen from Baltimore in the summers to continue to work with Born, at least until 1933. Together they published a major review on the dynamic lattice theory of crystals, which appeared in the 1933 edition of the prestigious *Handbuch der Physik* (M. Born and Göppert-Mayer 1933, 623–794).

Göppert wanted a career in science as a full professor. She recognized that such an aspiration had a very low probability if she remained in Germany. This followed from her knowledge that neither Noether, nor Lise Meitner, nor her good friend Sponer ever achieved a full university professorship in Germany (McGrayne 1993, 184–191).[11]

On 1 April 1930, Göppert-Mayer and her husband moved to Baltimore, Maryland, where Mayer held an assistant professorship at Johns Hopkins University. Her summer visits to Born in Göttingen ceased in 1933. Social and political realities in Germany resulted in forced migrations of many academics. Following the 7 April 1933 enactment of the Law for the Restoration of the Professional Civil Service, almost all non-Aryan civil servants (including tenured university professors) were removed from their positions in Nazi Germany. Born left Göttingen to take a position in the United Kingdom (H. Born and M. Born 1962). Franck, the recipient of the 1925 Nobel Prize in physics, quit his university professorship in protest against Nazi racial policies and emigrated to the United States (Lemmerich 2007).

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[11] That plan did not materialize in the United States for many decades. In the United States, Göppert-Mayer spent many years working as a volunteer in the physics departments of Johns Hopkins University, Columbia University, and as a voluntary associate professor and later as a voluntary professor at the University of Chicago (McGrayne 1993). At the same time, her husband working at the same institutions moved up the academic ranks to full professor. In 1956, she was elected to the National Academy of Sciences. Finally in 1960, she accepted a full professorship with pay at the University of California, San Diego. In 1963, Eugene Wigner, Göppert-Mayer and Johannes H. D. Jensen shared the Nobel Prize in Physics (Göppert-Mayer 1948; 1955; McGrayne 1993).

## 8.3 What Was the Role of Paul Dirac in Göppert's Dissertation Research?

### 8.3.1 Dirac's 1927 Publications

Three of Dirac's 1927 publications had a great influence on Göppert-Mayer's dissertation work (Dirac 1927a; 1927b; 1927c). She directly acknowledged Dirac's contribution to her research in her 1931 Göttingen dissertation and in her chapter on dispersion theory in *Elementare Quantenmechanik* (M. Born and Jordan 1930, 404–408; Dirac 1927b; 1927c). In the latter book chapter, a footnote states that the considerations in her section follow from Dirac's paper on the quantum theory of the emission and absorption of radiation and from Dirac's paper on the quantum theory of dispersion (Dirac 1927b; 1927c; Göppert-Mayer 1930). Furthermore, in their preface to *Elementare Quantenmechanik*, Born and Jordan state that Göppert contributed sections on Dirac's theory of emission, absorption and dispersion (M. Born and Jordan 1930, VII–VIII). In this section, I examine Dirac's contributions and evidence of his influence on Göppert's dissertation research.

### 8.3.2 Dirac's Paper on the Emission and Absorption of Radiation (Dirac 1927b)

Dirac states that the mathematical development in this paper on emission and absorption of radiation follows from his previous paper on the general transformation theory of quantum matrices (Dirac 1927a). In this paper, Dirac proceeds as follows: he considers an atom interacting with a field of radiation, which is confined to a cavity, to have a discrete set of degrees of freedom (Dirac 1927b). Dirac considers a finite cavity to enclose the radiation to establish a relationship between the number of light quanta per stationary state and the intensity of the radiation. He restricts the treatment to the non-relativistic case. In the absence of interaction between the atom and the radiation, the Hamiltonian consists of two terms: the field and the atom. In the presence of interaction, a third term from classical theory would be added to the Hamiltonian. From this formulation, Dirac derives the "correct" results for the action of the radiation and the atom on each other. Thus he derives the "correct" laws for the emission and the absorption of radiation and the "correct" values for Einstein's A and B coefficients (Einstein 1916).

### 8.3.3 Dirac's Paper on the Quantum Theory of Dispersion (Dirac 1927c)

Initially, Dirac explains that while the new quantum mechanics uses analogies found in classical theory, it cannot be applied to a class of problems where the analogies are obscure, for example, the problems of resonance radiation and the widths of spectral lines. Dirac proposes that the radiation field can be treated as a dynamical system composed of harmonic components with energies and phases, where each one is a harmonic oscillator. The interaction of this field with an atom can be described by a Hamiltonian function. Dirac then requires the use of perturbation methods to solve the Schrödinger equation. Dirac shows through the use of second-order perturbation theory that a double process can occur: first a transition from the initial state to an intermediate state, and then a transition from the intermediate state to the final state. Each of these processes does not conserve energy, but energy is conserved in the total process consisting of the two transitions, for example, from the initial to the final state in a double process. Dirac resolves the electromagnetic field into its components of plane-polarized, propagating waves, with each component of a definite frequency, direction, state of polarization. He confines the radiation to a cavity to discretize the number of components. Then, he formulates the Hamiltonian function in terms of a vector potential that describes the interaction of the field with the atom, which he considers a single electron in an electrostatic field with a potential. For the case of resonance, Dirac assumes a range of frequencies of the incident radiation, and he calculates the equations for the probability of the emission and the absorption of light quanta.

I now elucidate some of the details of his paper on dispersion theory (Dirac 1927c).

1. The basic idea of Dirac's theory of radiation is to describe the total system of radiation and the atom as the sum of three terms: the first term represents the energy of the atom, the second is the electromagnetic energy of the radiation field, and the third term is the interaction energy of the atom and the radiation field. In the absence of the third term, the atom could neither absorb nor emit radiation. Initially, Dirac decided not to consider the radiation in infinite space, but to represent the radiation as confined to a cavity, of finite volume (V) and with perfectly reflecting walls. Later, the cavity would expand to become infinite, and that would represent the radiation in free space. Then, the oscillations of the confined electromagnetic field are represented as the superposition of a finite number of fundamental vibrations; each one corresponds to a system of standing waves. The electromagnetic field of a monochromatic, plane standing wave in the cavity can be described by a vector potential. Next, the Hamiltonian of the atom

and the radiation field are described. The electromagnetic energy of the radiation field can be shown to have the same Hamiltonian as a system of uncoupled harmonic oscillators. The Hamiltonian for the total system of atom and radiation field is the sum of three terms: for the radiation field, for the atom, and the term of the interaction of the radiation and the atom. The last interaction term is the coupling term for the atom and the radiation field. Then, Dirac develops his time-dependent perturbation theory to calculate the probabilities of transitions of energy for the atom and for the radiation field. This is studied for a variety of cases: absorption, emission and induced emission.

2. Dirac uses a semiclassical treatment; the electromagnetic field is treated classically and the atoms with which the field interacts are treated quantum mechanically. The semiclassical approach "correctly" describes absorption and induced emission, but it fails to "correctly" describe the influence of the atoms on the electromagnetic field.
3. In the mathematical description of a plane linear-polarized monochromatic wave that is resolved into its Fourier components, there appears the frequency of the wave, an amplitude which is a complex vector, and two complex components of the wave amplitude; they are each multiplied by a unit polarization vector, which represents the two independent states of linear polarization.
4. To make the number of degrees of freedom discrete, Dirac assumed that the radiation field is confined to a cavity. According to Dirac's theory, radiation in a cavity can be described by giving the amplitude of each standing wave at a particular time; therefore, the amplitude can be considered a coordinate that follows the laws of quantum mechanics. In his theory of the interaction of atoms and radiation, he calculated the probabilities of both induced emission and spontaneous emission (no radiation present). In addition, it provided a new theory for dispersion and light scattering.
5. In the treatment of an atom and its interaction with a radiation field, the process of the absorption of a photon by an atom involves the increase in the energy of the atom by a quantum of energy, and the decrease of the harmonic oscillators comprising the radiation field by a quantum of energy. The combined energies of the electron and the radiation oscillators follow the law of conservation of energy.
6. Dirac's perturbation theory included two cases: time-dependent and time-independent perturbations. An example of the former case is the calculation of absorption of light or the induced emission of light by an atom in a radiation field.

7. Dirac's time-dependent perturbation theory can be used to calculate transitions between discrete energy levels, as well as in physical systems with continuous energy levels. For example, in particle collisions, the eigenfunctions of the free particles, that is, electrons colliding with atoms, are described as plane waves, and the energy of the particles is not quantized, but can take different positive values. If the particles are now confined to a box, the eigenvalue or the energy of the particle is now quantized. As the size of the box increases to infinity, the free particle eigenfunctions and energy eigenvalues approach those of the free particle. For a free particle in a box, the quantized energy eigenvalues can be calculated by perturbation theory for discrete energy levels. Then the size of the box is increased to infinity, and the result obtained is valid for continuous energy levels.
8. Raman scattering is another example of a two-photon process. A photon is absorbed and another photon is emitted; the atom makes a transition from the initial to the final state. The energy difference between the initial and the final states is equal to the energy difference of the two photons. Second-order perturbation can be used to calculate the Raman transition probabilities, which are the square of the transition amplitudes for the process. Time-dependent perturbation theory is required to calculate the rates of the transitions.
9. Dirac states that the exact interaction energy of the field and the atom is too complicated, therefore he uses the dipole energy. That approximation results in a divergent series that appears in the calculation. In his calculation of dispersion and resonance radiation, there is no divergent series, but when he attempts to calculate the breadth of a spectral line, a divergent series appears.

As we shall see in the following section, many of these aspects of Dirac's 1927 publications were directly incorporated into Göppert's Göttingen dissertation.

## 8.4 Reconstruction of Göppert's Göttingen Dissertation

The origin of Göppert's dissertation research were two publications by Oldenberg and Franck on electronic excitation of atoms due to inelastic collisions with electrons and the subsequent luminescence (Oldenberg 1928; Franck 1928). The significance of these experiments is that they demonstrated the discrete energy levels of atoms. The inelastic collisions of electrons and atoms can result in the transfer of energy to the atoms and can excite the atoms without ionizing them. These experiments were conducted at the Second Institute of Physics, and they provided Göppert with an opportunity to seek a theoretical explanation for these purported two-photon findings.

Next, I review Oldenberg's and Franck's 1928 papers (Franck 1928; Oldenberg 1928). The basis of Oldenberg's experiments was the question: could an atom become excited (its electrons are raised to higher energy states than the ground electronic state) through a single act of collision between electrons and an incident light field? He also discussed the concept that two light quanta can work together in one elementary act to excite an atom or molecule, for example, the Smekal-Raman effect (Smekal 1923).

Oldenberg produced experimental evidence on the broadening of resonance lines of mercury atoms when the excited atoms collide with slow particles multiple times. He showed that the excitation energy of the mercury atoms can be transferred as kinetic energy to the particles, and the difference frequency is radiated as light. The publication contains an equation that shows how two light quanta, with two different frequencies, can work together in a single elementary act to excite an atom (double absorption or two-photon absorption). In the second section of Göppert's Göttingen dissertation, she constructed the theory of "the working together of light and collisions [electrons] in one elementary act" (Göppert-Mayer 1931, 288). Her theoretical analysis agrees with Oldenberg's previous experimental results (Oldenberg 1928).

Franck focused his research program on atomic physics and spectroscopy.[12] In Göttingen, Franck continued to experiment with collisions of fast electrons and atoms. He explored the effect of the velocity of colliding electrons on the spectral lines of atoms. He studied the ionization of atoms due to collisions with slow and fast electrons and the subsequent luminescence that was observed. According to Franck (1928), this process is due to the recombination of ions and electrons.

Göppert worked on the theory of atom-photon interactions. Building on Hans Kramers and Werner Heisenberg's dispersion theory, and Dirac's time-dependent perturbation theory, she developed analytical expressions of the transition probability for multi-photon absorption and stimulated emission, as well as Raman scattering processes (Kramers and Heisenberg 1925).[13] Note that in her 1929 paper, she stated that Dirac's dispersion theory described not only the Ra-

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[12] In 1926, Franck and Gustav Hertz received their Nobel prize in physics. Franck was awarded the Nobel for his work during the 1912–1914 period, specifically the Franck-Hertz experiment based on the inelastic scattering of electrons by mercury atoms in the gas phase. Franck and Hertz demonstrated that a collision between an electron and an atom can result in a transition of the atom from its ground state to a stationary state of higher energy; in the process, the electron loses an equal amount of energy (Franck and Hertz 1914). Their experiment provided an important confirmation of the quantization of an atom's energy levels.

[13] To obtain a sense of the physical theories and techniques that were in use at the time of Göppert's graduate research, I recommend that the reader examine *Elementare Quantenmechanik* (M. Born and Jordan 1930).

man effect but also the reverse process in which two photons act together in a single elementary event to promote an atom from the ground state to an excited state (Dirac 1927c; Göppert 1929).

What theoretical and mathematical techniques did Göppert use in her dissertation research that followed Dirac's previous publication (1927c)? To address this question, I surveyed physics and mathematics books published in the 1920s. In particular, the book series edited by Born and Franck entitled *Struktur der Materie in Einzeldarstellungen* (1925), and a book by Franck and Jordan (1926) on collisions. Although it is likely that she read these volumes as a student, I refer to Göppert's publications in which she explicitly cites experimental works from the Franck group and Dirac's theoretical papers as major influences on her dissertation research. In particular, a careful analysis of her dissertation reveals four similarities with Dirac's dispersion paper (Dirac 1927c). The first section of her dissertation is concerned with two light quanta working together in one elementary act (Göppert-Mayer 1931, 273–284). The four similarities are listed below in extracts from Göppert's dissertation:

1. With the help of Paul Dirac's dispersion theory, the probability of an analogous Raman effect process is calculated, namely the simultaneous emission of two light quanta. It is shown; that a probability exists for an excited atom to divide its excitation energy into two light quanta [...]. If an atom is irradiated with light of a lower frequency than the frequency associated with an eigenfrequency of the atom, there additionally occurs a stimulated double emission [...]. Kramers and Heisenberg (1925) calculated the probability of this last process in a corresponding manner [273].
2. The reverse process is also considered, namely the case that two light quanta, whose sum of frequencies is equal to the excitation frequency of the atom, work together to excite the atom. It is further investigated how an atom responds to colliding particles, when at the same time it has the possibility of spontaneously emitting light. Oldenberg (1928) experimentally found a broadening of the resonance lines of mercury, when he allowed the excited atoms to collide many times with slow particles [273]. For this process, an equation is derived here that is analogous to the Raman effect or double emission [274]. Finally, in relation to a study by James Franck (1928), an attempt is made to explain the behavior of the intensity of excitation of spectral lines, induced by collision [of atoms] with fast electrons in such a double process [274]. The calculation shows a probability for such a process, the nature of which will be discussed [275].
3. The following calculation is closely associated with the work of Dirac on emission, absorption, and dispersion [275].

4. Let us consider the interaction of an atom with a [electromagnetic] radiation field. To make the number of degrees of freedom countable, think of the radiation contained in a cubic box of volume V, which constrains the light waves to the condition of periodic repetition [standing waves]. Later this box will be assumed to be infinitely large. Such a radiation field is equivalent to a system of uncoupled harmonic oscillators. The radiation can be decomposed in plane, linear polarized waves, let A be the vector potential […] [276].[14]

Perusal of her Göttingen dissertation indicates that Göppert made use of the following assumptions and techniques:[15]

1. the confinement of the radiation field in a cavity so that the number of the degrees of freedom can be discrete,
2. the use of the vector potential [277],
3. the description of the total Hamiltonian function consisting of three components: the Hamiltonian of the radiation field (the uncoupled harmonic oscillators), the Hamiltonian of the atom, and the Hamiltonian of the interaction between the atom and the radiation field [277], the electric dipole approximation in which it is assumed that the wavelength of the light is much larger than the atom's diameter, that is the assumption that the electromagnetic field is constant over the atom's diameter [277–278],
4. the use of second-order, time-dependent perturbation theory [278–284],
5. the use of two-photon transitions via virtual intermediate states [278–284], and
6. the "method of variation of constants," mentioned by Göppert [280].

The state of an atom is represented by an expansion in terms of the unperturbed energy eigenfunctions. The Hamiltonian operator is different from the true Hamiltonian by a very small term, which is the perturbation. The method of variation of constants derives its name from the fact that the constant coefficients used in the expansion of the wave function, in terms of the true energy eigenfunctions, vary with time.

The second part of Göppert's Göttingen dissertation addresses the way light and collisions (electrons) work together in one elementary act (Göppert-Mayer 1931, 284–294). First, she defines the Hamiltonian function of the total system in which the interaction energy is separated into two parts: one term is the interaction of the atom and the radiation, and the second term is the interaction between

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[14] Page numbers in square brackets refer to Göppert's dissertation, published in *Annalen der Physik* (Göppert-Mayer 1931). The quotations 1–4 here are translated from German by the author (Masters 2010).

[15] Page numbers in square brackets in this list of six assumptions and techniques refer to Göppert-Mayer (1931, 277–284).

the atom (nucleus) and the electron, which is approximated by the Coulomb field. The electron waves are enclosed in a cavity with the same conditions as for the radiation: periodic standing waves. In the first case, she assumed only one atom and one electron in the cavity and no radiation; thus, there are only emission processes. She calculated the probabilities for transitions in the state of the atom due to light alone, and performed a similar calculation for the transitions due to electron collisions alone. Then, she used second-order perturbation theory to study how light and collisions work together. The second part of her Göttingen dissertation was stimulated by the experimental results of Franck's research group, and it confirmed many of their findings (Göppert-Mayer 1931, 284–294).

The significance of this careful reconstruction of her Göttingen dissertation, together with a thorough comparison of the two papers that Dirac published in 1927, demonstrates that Göppert not only used and cited Dirac's papers, but the extent to which she incorporated theoretical techniques from those two papers is significant. Previously, this incorporation of Dirac's work into her Göttingen dissertation has either not been described or has been ignored in the literature on the history of quantum mechanics.

## 8.5 What Was Known and What Did Göppert Contribute in Her Dissertation Research?

Göppert and Weisskopf were contemporary doctoral students under Born. In this section, I compare the influence of Dirac on Göppert's research and the influence of Wigner on Weisskopf's research. My studies of both Göppert's and Weisskopf's Göttingen dissertations raised the question of the level of originality required at that time for a doctoral dissertation. Both dissertations are at approximately the same level of originality. It is important to understand the role of the dissertation and habilitation to put this question of originality into perspective.

Göppert's Göttingen dissertation relied on second-order, time-dependent perturbation theory. Since perturbation theory was a major mathematical technique in her doctoral theoretical research, it is necessary to look into its antecedents. What are the sources of this theory and how did approximation methods from celestial mechanics find a place in quantum mechanics?

The early development of these perturbation techniques derived from problems in astronomy (Masters 2008b, 36–41). To solve three-body problems or n-body problems, a number of techniques were developed. When the Hamiltonian for the exact problem is known, and it differs slightly from the Hamiltonian for the less complex soluble problem, then approximation or perturbation techniques were derived. The fundamental basis of all the perturbation methods is that the solutions of the perturbed system are only slightly different from the solutions (the integrated form of the equations of motion) of the equations of motion of the unperturbed system that are already integrated. The main mathematical problem to overcome is that when series expansions were used as approximations of a function, they did not always converge or sum to a finite term; in many cases they diverged to infinity (M. Born 1924; 1925).

In the winter semester of 1922–1923, Born arranged a course on perturbation theory at his institute in Göttingen. In 1922, Paul Epstein independently developed his form of perturbation theory with applications to quantum mechanics (Epstein 1922a; 1922b; 1922c). Earlier in 1916, Epstein developed a perturbation method to treat the helium atom (Epstein 1916). His method was based on similar work by the French astronomer Charles Eugène Delaunay. Born recognized that the perturbations in his theory were similar to the degenerate perturbations in celestial mechanics called "secular perturbations" (M. Born 1924; 1925). The word "secular" was first used in classical mechanics to describe a perturbation that has a very slow and cumulative effect on the orbit of a planet.

Much of the later progress on perturbation theory stems from the works of Born, Schrödinger, Epstein, and Dirac; these methods built on the earlier work of Henri Poincaré. The early formulations of perturbation theory were modified for their application in both old and new quantum theories (Masters 2008b, 36–41). In 1926, Schrödinger published five papers on his newly-derived wave mechanics and some applications to the "Stark effect" of the "Balmer lines." He developed his time-dependent wave equation and was able to calculate the intensities and polarization of the "Stark effect" on the "Balmer series" of electronic transitions in the hydrogen atom. His expression for the energy shifts is equivalent to that derived by Epstein. In 1926 and 1927, Dirac developed his time-dependent perturbation theory (Dirac 1926; 1927b). Dirac's time-dependent theory was the basis of Göppert's dissertation.

In the second part of her Göttingen dissertation, she calculated the probabilities of the combined action of light and electron collisions in the electronic transitions of atoms. Göppert's dissertation contained the theoretical basis for two-photon absorption and emission processes; she called the effects "double absorption" and "double emission."[16]

The probability of the two-photon process is proportional to the square of the light intensity, and the rate constant for the two-photon process is very low

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[16] It is significant that in Born and Jordan's *Elementare Quantenmechanik* (1930), section 74 on the absorption and emission of radiation by atoms, they cite in the footnote on page 400 Dirac's 1927b and 1927c papers, and they state that the theoretical development in the section follows Dirac's work. In section 75 on scattering and dispersion, a footnote states the text is analogous to Göppert's 1929 "Die Naturwissenschaften" paper, but in fact it is largely taken from Göppert's 1931 Göttingen dissertation. A careful comparison of section 75, her 1929 publication, and her 1931 Göttingen dissertation clearly indicates that an early draft of her Göttingen dissertation is the basis of section 75.

compared to a single-photon process that has a rate constant that is proportional to the light intensity. Göppert predicted nonlinear interactions between light and matter mediated by multi-photon processes. Furthermore, she showed that in a double transition or a two-photon transition via intermediate states or a virtual state, each part of the transition does not obey the conservation of energy law; however, the total transition from the initial state to the final state follows the law of conservation of energy. This is exactly what Dirac showed in his dispersion paper.

Weisskopf and Göppert were contemporary doctoral students of Born in Göttingen. It is interesting to explore Dirac's influence on Weisskopf's research and to compare Dirac's influence on the two doctoral students. Perusal of Weisskopf's Göttingen dissertation and his biography provide additional support for the mutual interaction of the experimental and theory groups in Göttingen's physics institutes, as well as the effect of the visitors on both Göppert's and Weisskopf's research programs (Weisskopf 1931; 1991).

Although Weisskopf arrived in 1928, both published their Göttingen dissertation in the same 1931 volume of *Annalen der Physik*. In his 1991 biography, Weisskopf cites the people who had seminal influences on his research in Göttingen: Franck, the experimental physicist who could accurately predict the results of an experiment or a theoretical calculation; Hilbert and especially Courant, who taught Weisskopf advanced mathematics; the three young teachers, Walter Heitler, Lothar Nordheim and especially Herzberg who taught the course "Introduction to Quantum Mechanics," which included the latest developments in the field (Weisskopf 1991).

According to Weisskopf, it was Dirac's 1927 paper, "The Quantum Theory of Emission and Absorption of Radiation" (Dirac 1927b), which was published prior to Weisskopf's arrival in Göttingen, that influenced Weisskopf's choice of a thesis problem (Weisskopf 1991). Dirac's paper demonstrated how to calculate the rates of the emission and absorption of light from an atom, but not how to calculate the line width of the transitions; Weisskopf decided to investigate the line width shapes for the transition from the first excited state to the ground state.

Born had a stroke shortly before Weisskopf arrived in Göttingen in 1928; therefore, Weisskopf turned to Wigner for mentorship. Wigner often visited Göttingen from Berlin. Together, they started with Dirac's 1927 paper on radiation (Dirac 1927b) and developed a novel theory that was published in two papers in 1930 (Weisskopf and Wigner 1930; 1930). Their first paper was entitled "Calculation of the natural line width due to the Dirac theory of light" (Weisskopf and Wigner 1930) in which the authors twice credit Dirac for previously publishing the techniques used in their present calculations for the interaction of light and matter. These include standing waves of radiation in a cavity and the matrix methods to calculate transitions. The authors also wrote a footnote crediting Göppert for a similar calculation published in her 1929 paper (Göppert 1929).

In their second paper, Weisskopf and Wigner extended their calculation of the natural line width due to the Dirac theory of light interacting with an atom. The authors found that their quantum mechanically calculated line width of a harmonic oscillator coincides perfectly with the line width as calculated by classical theory (Weisskopf and Wigner 1930).

Weisskopf and Wigner's two 1930 publications incorporated the assumption "that all the atomic states that were not directly involved in the emission of radiation could be neglected" (Weisskopf 1991, 43). According to Weisskopf, this technique differed from the perturbation techniques, "which assumed that the interaction between the atom and the light is very small" (Weisskopf 1991, 43).

This so-called Weisskopf-Wigner theory was later used to solve other problems in quantum field theory (Weisskopf 1991). Because this joint research could not be submitted as his dissertation work, Weisskopf used the same theoretical approach to solve the problem of the re-emission of light absorbed from atoms. The title of his Göttingen dissertation is "Zur Theorie der Resonanzfluoreszenz" (Weisskopf 1931). Weisskopf's selection of this topic was also influenced by the work of Robert Wood, an experimental physicist who worked at Johns Hopkins University and published spectroscopic data on resonance fluorescence (Wood and Ellett 1924). Weisskopf discussed Wood's spectroscopic studies with Franck, whose spectroscopic group was involved with measurements of line widths (Weisskopf 1991). At the end of his Göttingen dissertation, Weisskopf thanked Born, Franck and Wigner for many supportive suggestions and discussions; these thanks provide further evidence of the interactions between the experimental group headed by Franck and the theoreticians Born and Wigner (Weisskopf 1991).

In summary, a study of Göppert's and Weisskopf's Göttingen dissertations indicates the fundamental influences of Dirac's prior publications. They also illustrate the communication between Franck's experimental groups and these two graduate students in Born's theory group.

## 8.6 Conclusion

From the previous discussion, I conclude that Dirac's 1927 publications had a substantial influence on Göppert's and Weisskopf's doctoral research, on their 1931 Göttingen dissertations, and on their publications of 1929 and 1930, respectively. Although it was not previously described, I suggest that Göppert's research borrowed more heavily from Dirac's theoretical techniques (with appropriate citations to Dirac) than did Weisskopf. In fact, my comparison of the dissertations and Dirac's previously published papers indicate that Göppert borrowed Dirac's theoretical techniques to an extraordinary extent.

The question remains: why was Göppert able to predict two-photon transitions and calculate their probabilities for several cases? I propose the following answer. Oldenberg suggested that the experimental findings are indicative of a two-photon process. In addition, Dirac had provided the theoretical techniques to calculate the probabilities for two-photon transitions via virtual states in his dispersion paper of 1927. Göppert possessed superb mathematical skills, as well as a deep insight into experimental physics, was able to perform a synthesis of the works of Oldenberg and Dirac, and was able to work through the detailed quantum mechanical calculations that resulted in a theoretical understanding of Oldenberg's results.

She calculated the transition probabilities for two-photon absorption, two-photon emission and two-photon Raman processes for the Stokes and the anti-Stokes cases. With the invention of the laser, her theoretical predictions of two-photon processes of light absorption and emission would later be verified (Boyd 2008; Maiman 1960; Masters and So 2008).

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