

## Erwin Schrödinger and the Rise of Wave Mechanics.<sup>1</sup> I. Schrödinger's Scientific Work before the Creation of Wave Mechanics

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*This article is in three parts. Part I gives an account of Erwin Schrödinger's growing up and studies in Vienna, his scientific work—first in Vienna from 1911 to 1920, then in Zurich from 1920 to 1925—on the dielectric properties of matter, atmospheric electricity and radioactivity, general relativity, color theory and physiological optics, and on kinetic theory and statistical mechanics. Part II deals with the creation of the theory of wave mechanics by Schrödinger in Zurich during the early months of 1926; he laid the foundations of this theory in his first two communications to Annalen der Physik. Part III deals with the early applications of wave mechanics to atomic problems—including the demonstration of equivalence of wave mechanics with the quantum mechanics of Born, Heisenberg, and Jordan, and that of Dirac—by Schrödinger himself and others. The new theory was immediately accepted by the scientific community.*

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### 1. SCHRÖDINGER'S FAMILY BACKGROUND AND SCHOOL EDUCATION

Erwin Schrödinger, the spiritual and scientific heir of Ernst Mach, Ludwig Boltzmann, and Friedrich Hasenöhl, was born in Vienna on August 12, 1887, the son of Rudolf Schrödinger, who owned a linoleum business inherited from the family, and his wife Georgina. Though he ran his

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business successfully and profitably until he died in December 1919, Rudolf Schrödinger did not have a great interest in it. Rudolf was a cultivated man; after studying chemistry, he occupied himself devotedly with Italian painting and in drawing and etching landscapes. Then he turned his attention to the study of plants, and wrote a series of papers on the phylogeny of plants.<sup>(1)</sup>

Rudolf Schrödinger had married Georgina, the second of the three daughters of his former teacher, Alexander Bauer, professor of chemistry at the *Technische Hochschule* in Vienna. Erwin described his mother as follows: "My mother was very nice, with a cheerful character; she was of poor health and hopeless toward life, but also unassuming."<sup>(1)</sup> However, she greatly cared for her only child, who would always retain for her a tender memory and great affection. Her mother was English, and young Erwin visited England and his grandmother when he was a boy. He learned English very early in life, and would later master this language nearly as well as his native German. However, the decisive influence on Erwin's education was exerted by his father. "For the growing son he was a friend, a teacher, and an untiring discussion partner and a court of appeal for everything which might interest me," recalled Schrödinger.<sup>(1)</sup> Much later, after World War I, when Erwin wanted to marry and doubted whether he could support a family in an academic position, he asked his father: "Could you take me into your business?" Upon which Rudolf Schrödinger replied: "No, my dear, you won't go into this business. I don't want you to do this. You stay at the university and you go on [with your academic career]."<sup>(2)</sup>

The young Schrödinger did not go to an elementary school; instead he was taught at home by a *Volksschullehrer* until his eleventh year. From 1898 to 1906 he attended the *Öffentliches Akademisches Gymnasium* in Vienna.<sup>(3)</sup> This was a humanistic *Gymnasium*, which concentrated heavily on Greek and Latin, but where science was also taught at a high level. Erwin was a good student in all subjects; he loved mathematics and physics, as well as the rigorous logic of Greek and Latin grammars, but he disliked memorizing historical and biographical data and facts. According to his classmates, he possessed great quickness and presence of mind. He loved the German poets and writers, especially the dramatists. The love for drama made the student Schrödinger an addict of the famous *Burgtheater* in Vienna. In particular he adored the plays of Franz Grillparzer. He retained his interest in literature to the end of his life, and even published a book of poems of his own.<sup>(4)</sup> He was a talented linguist, who could speak many languages, presenting his lectures in German, English, French, or Spanish, as necessary; he also used to translate Homer from the original Greek into English, and old Provençal poems into German. Though he did not much appreciate music, he possessed a great understanding of old and

modern painting and enjoyed himself in his leisure time by working on sculptures. His love of Greek and Latin languages provided him access to classical literature and culture of antiquity, especially the philosophy of Greeks. Thus already during his last *Gymnasium* year he prepared a notebook on an account of Greek philosophy from Thales of Miletus to Plato. Schrödinger would return to the subject of the philosophy of the ancient Greeks again and again in his life, being attracted by its intimate and basic relation to the origin of science in Europe. Thus, for example, he would devote his *Shearman Lectures*, delivered in May 1948 at University College, London, to demonstrate the continuity of the Greek philosophical tradition in modern science, including relativity and atomic theory.<sup>(5)</sup> His great interest in the Greek philosophers, especially those of the Ionic school, led him to a great natural love for physics and mathematics, and when he graduated with his *Maturat* from the *Gymnasium* in summer 1906, he decided to study these fields at the University of Vienna.

## 2. STUDENT AT THE UNIVERSITY OF VIENNA

In the winter semester of 1906/1907 Erwin Schrödinger enrolled in the University of Vienna, as a student of “mainly physics and mathematics, and [as minors] of chemistry and astronomy.”<sup>(3)</sup> He attended a full complement of courses in mathematics, theoretical and experimental physics, chemistry, and astronomy during the following four years.<sup>(6)</sup> His teachers were Franz Mertens (differential and integral calculus, algebra and probability calculus, and definite integrals), Gustav von Escherich (probability theory, theory of functions, definite integrals, and variational calculus), Gustav Kohn (spherical trigonometry, algebraic curves, analytic geometry, and continuous groups), Emanuel Czuber (differential geometry), Julius Ferdinand Hahn (meteorology), Josef von Hepperger (spherical astronomy and the three-body problem), Wilhelm Wirtinger (theory of functions, differential equations, and mathematical statistics), Joseph Nabl (screw geometry), Lothar von Schrutka (higher algebra), Zdenko Hanns Skraup (general and inorganic chemistry and organic chemistry), Viktor von Lang and Franz Exner (experimental physics), Anton Lampa (acoustics), and Friedrich Hasenöhl (mechanics, including Hamilton’s principle of least action; mechanics of continua; heat theory, including thermodynamics, kinetic theory, and statistical mechanics; optics; and electrodynamics). Schrödinger kept the lecture notes of most of his courses, and these are preserved in his *Nachlaß*. In spite of his family relationship with chemistry—via his maternal grandfather Alexander Bauer—Schrödinger would never in his later career show particular interest

in chemical problems. However, he would be attracted, especially during the Vienna period, to problems of meteorology—such as atmospheric electricity. The central field of Schrödinger's studies had undoubtedly been physics, and his main teachers in this field were Franz Exner, Fritz Hasenöhl, and Viktor von Lang. Exner and Hasenöhl had the greatest influence on Schrödinger.

Friedrich Hasenöhl had been a student of Ludwig Boltzmann. Boltzmann had recommended Hasenöhl to Heike Kamerlingh Onnes for the position of an assistant at Leyden upon the completion of his studies in Vienna, and he spent the year 1898/1899 in Holland, where he became good friends with Kamerlingh Onnes and Hendrik Lorentz. Back in Vienna, Hasenöhl got his *Habilitation* at the end of the year 1899. The young Hasenöhl soon won a reputation as an excellent teacher. The special care which he devoted to the preparation of his lectures attracted to him a host of faithful auditors (among others, Paul Ehrenfest, Felix Ehrenhaft, and Gustav Herglotz), and it characterized his entire later teaching. His research in theoretical physics also won Hasenöhl the recognition of the scientific community in Austria and abroad. In 1905 Hasenöhl was appointed to an extraordinary professorship of general and technical physics at the *Technische Hochschule* in Vienna, and two years later he succeeded Ludwig Boltzmann in the chair of theoretical physics at the University of Vienna. Hasenöhl fully justified the expectations placed in him; he became a worthy and effective propagator of Boltzmann's ideas, and he even surpassed his former teacher in creating a flourishing school of theoretical physics in Vienna. Thus he counted among his students Ludwig Flamm, Karl Herzfeld, Friedrich Kottler, Erwin Schrödinger, and Hans Thirring.

When Schrödinger began his studies at the University of Vienna in the winter semester of 1906/1907, Ludwig Boltzmann had just committed suicide. Some of his students had left the University of Vienna, like Paul Ehrenfest and Lise Meitner<sup>(7)</sup>; or, like Philipp Frank and Ludwig Flamm, they completed their studies with other professors. Still Boltzmann's influence remained very much alive. As Schrödinger recalled nearly a quarter of a century later: "The old Vienna institute, which had just mourned the tragic loss of Ludwig Boltzmann, where Fritz Hasenöhl and Franz Exner worked and where many other students of Boltzmann came and went, provided me with a direct insight into the ideas of that powerful mind. His world of ideas may be called my first love in science. No other personality has ever since so enraptured me or will do so in future."<sup>(8)</sup>

Boltzmann's world of ideas, which caught the imagination of the young Schrödinger, implied of course—as its central point—the atomic structure of matter. Fritz Hasenöhl, Boltzmann's former student,

advocated the atomic hypothesis firmly; Franz Exner, the friend and successor of Joseph Loschmidt, also supported the atomic hypothesis. As a student, Schrödinger did not hear much about relativity and quantum theories, but he did learn about some modern topics, for example, in Karl Przibram's lectures on "*Die neueren Anschauungen über die Konstitution der Materie*," delivered in the winter semester of 1908/1909 and continued in the following summer semester of 1909.<sup>(9)</sup> Przibram's lectures covered an enormous variety of topics and results—from the kinetic theory of matter and Boltzmann's collision equation and its applications to the Zeeman effect and the laws of radioactive decays.

Beginning in 1906, Schrödinger sat through a four-year cycle of daily lectures given by Friedrich Hasenöhl on theoretical physics. The emphasis was on Hamiltonian mechanics and the theory of eigenvalue problems in the physics of continuous media. The direction of Hasenöhl's lectures is indicated by one of his articles in the Boltzmann *Festschrift* of 1904 entitled "On the Application of Hamilton's Partial Differential Equation to the Dynamics of Continuously Distributed Masses." In this paper, Hasenöhl claimed that he was making the first attempt to employ Hamilton's partial differential equation in the solution of problems of motion in a continuous medium. He selected the simplest example—that of the vibrating string—and obtained a solution using Hamiltonian methods.<sup>(10)</sup> While he did not derive a wave equation—the method permitted a solution *without* deriving a wave equation—Hasenöhl was obviously headed in the right direction for Schrödinger.

Although by the end of his university studies Schrödinger had developed a marked interest in theoretical problems, he did not consider himself a theoretical physicist yet. Indeed, he carried out his first scientific research at Franz Exner's institute. It was an experimental investigation "On the Conduction of Electricity on the Surface of Insulators in Humid Air," a paper which was communicated on June 30, 1910 to the Imperial Academy of Sciences and appeared later in the *Sitzungsberichte* of the Academy.<sup>(11)</sup> It grew from the interest that existed at Exner's institute in the problem of atmospheric electricity. As Schrödinger noted: "Starting from the known fact that electrostatic experiments succeed badly in humid air, I have tried to investigate the influence of moisture on those insulating materials which are most often used in laboratories." Thus he took rods of ebonite, glass, polished amber, sulfur, and paraffin, wrapping their ends in tinfoil and connecting one end with an accumulator battery, the other with an electroscope. While in dry air, the electroscope showed no indication it was charged, but when under the influence of moisture, the surfaces of the rods became conducting. Schrödinger measured in particular the speed of charging the electroscope and derived from the results the electrical

resistance of different materials as a function of the humidity. He found finally that glass had to be considered the worst, and paraffin the best, insulator for measurements of atmospheric electricity.

Schrödinger submitted this research on the conductivity of insulators in moist air as his doctoral thesis to the philosophical faculty of the University of Vienna. His supervisor for the doctoral work was Egon von Schweidler. Schrödinger was then duly admitted to the necessary examinations for obtaining the doctorate, i.e., the *Haupttrigorousum* in physics and mathematics and the *Nebenrigorousum* in philosophy; he passed those in May 1910. In the fall of the same year he took leave of absence from the university to perform military service for a year.

### 3. SCHRÖDINGER'S EARLY SCIENTIFIC WORK

In October 1911 Schrödinger returned to Vienna from military service and obtained the position of a substitute assistant (*Aushilfsassistent*) at his old institute, i.e., Franz Exner's physical institute. After Egon von Schweidler left in the summer of 1911 to accept a professorship at Innsbruck, K. W. Fritz Kohlrausch became Exner's chief assistant. Shortly before Schrödinger started his new position, Kohlrausch became *Privatdozent* for physics at the University of Vienna. The experienced, senior experimentalist Kohlrausch was just the right person to organize, together with the more theoretically minded Schrödinger, the physical laboratory courses at Exner's institute. He also stimulated some of Schrödinger's research, especially on topics of atmospheric electricity and radioactivity, and later in color theory.

The first period of Schrödinger's scientific activity embraced less than three years, from the fall of 1911 to the summer of 1914. During this period he contributed ten papers on various topics of experimental and theoretical physics and completed a review article on dielectric substances for a physical handbook. His major fields included the study of the dielectric properties of matter, atmospheric electricity (both experimental and theoretical), and the theory of X-ray patterns (von Laue diagrams) and of dynamic point lattices. Schrödinger's first publications as the new assistant for experimental laboratory courses dealt with calculations within the kinetic theory of matter and electron theory, fields with which he had already become acquainted as a student. In his paper, "On the Kinetic Theory of Magnetism," Schrödinger suggested how an additional diamagnetic contribution to atomic moments, besides the one created by the electrons orbiting in the atoms, might arise.<sup>(12)</sup> The contribution to the theory of diamagnetic properties of metals constituted a nice application of

the theoretical methods which Schrödinger had learned as a student to physical ideas proposed by renowned senior physicists, such as Thomson, Lorentz, and Langevin. Schrödinger's was, of course, not the correct solution to the problem, as it was too early to think of the solution of any of the problems involving metal electrons before the arrival of the correct quantum statistics for electrons,<sup>(13)</sup> but it clearly showed the influence of Boltzmann's work.

Encouraged by the apparent success of his first paper on kinetic theory, Schrödinger pursued a more ambitious program. On October 17, 1912, less than four months later, he presented a second paper to the Vienna Academy of Sciences, with the title "Studies on the Kinetics of Dielectric Substances, the Melting Point, Pyro- and Piezo-Electricity."<sup>(14)</sup> Schrödinger addressed the ultimate goal in the first sentences of the introduction by stating: "While today the difference between the gaseous and fluid state, at least in principle, seems to have been solved and removed to a certain degree by van der Waals' theory, the same does not hold for the transition from the fluid to the solid state. The latter process indeed seems to be much more mysterious than the first one."<sup>(15)</sup> The mystery mentioned showed up in the fact that the transition from fluid to solid was not necessarily accompanied by a contraction in volume but rather by the occurrence of a regular crystal structure. Schrödinger thought that "this can certainly be explained by general thermodynamics; atomistics so far, however, has not provided a proper description."<sup>(15)</sup> As a scientific descendent of Boltzmann, he felt that this problem had to be attacked, and he believed he had in hand the key to a kinetic theory of solids.<sup>(16)</sup>

Schrödinger derived the stimulus for his proposed theory from an article of Peter Debye in Zurich on "Some Results of a Kinetic Theory of Insulators," published in a February issue of *Physikalische Zeitschrift*.<sup>(17)</sup> In it Debye had assumed that an extra term had to be introduced into the description of the effect of the electric field on a fluid substance; that is, the electric field  $E$  not only caused the elastically bound electrons in the molecules of the fluid to shift their positions (leading to a dielectric polarization  $P$ ) but also acted on "permanent dipoles of constant electric moment  $[m]$ ," existing in the interior of the insulating substances. He had thus obtained a temperature dependence of the polarization  $P$  according to the equation

$$P = \left( E + \frac{P}{3} \right) \left( \frac{3a}{T} + 3b \right) \quad (1)$$

with

$$a = \frac{Nm^2}{3k} \quad (2)$$

where  $N$  denoted the number of molecules per  $\text{cm}^3$  and  $k$  the Boltzmann constant. Hence the dielectric constant  $\varepsilon$  ( $= 1 + P/E$ ) satisfied the relation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{a}{T} + b \quad (3)$$

in which  $b$  described the temperature-independent term provided by the polarization of the bound electrons—the only terms considered so far—and  $a/T$  the new, temperature-dependent part arising from the permanent dipoles.<sup>(18)</sup> Debye had further noticed that the dielectric constant  $\varepsilon$  assumed a singular (infinite) value at a critical temperature  $T_k$ ,

$$T_k = \frac{a}{1 - b} \quad (4)$$

and concluded: “If the temperature  $T$  is decreased below  $T_k$ , the detailed theory shows that a polarization may exist in the interior of the body even when an external field is absent; that is, one would be able to observe then a residual dielectric polarization.”<sup>(19)</sup> However, he had immediately dismissed this possibility as being unrealistic, since the fluids turned into solids at temperatures considerably above  $T_k$ , Eq. (4), and therefore “the validity of the relation (3) ceases, since the molecules cannot rotate freely any longer.”<sup>(19)</sup> Still, Debye had pointed out the analogy of the temperature  $T_k$  for dielectric substances to the Curie temperature for ferromagnetic substances.

This last remark in Debye’s paper interested Schrödinger. He now suggested in particular the idea “that a certain... ‘critical’ temperature exists for each dielectric substance, below which spontaneous electrization must occur, and which is the exact analogue of the Curie point for ferromagnetic substances; and this critical temperature is identical with the melting temperature.”<sup>(20)</sup> He knew the theory of ferromagnetism, which Pierre Weiss had developed by generalizing Paul Langevin’s molecular-kinetic description of the magnetic properties of matter.<sup>(21)</sup> If one took Debye’s Eq. (1) as describing the electrical analogue of paramagnetism, then a generalized equation could be written down, namely,

$$P = 3b \left( E + \frac{P}{3} \right) + Nm \left( \frac{\cosh \alpha}{\sinh \alpha} - \frac{1}{\alpha} \right) \quad (5)$$

with

$$\alpha = \frac{m(E + P/3)}{kT} \quad (5a)$$



corresponding to Weiss' equation for para- and ferromagnetic substances. In the limit of small  $\alpha$  or of high temperatures, this equation passed over into Debye's Eq. (1), which in Schrödinger's theory accounted only for fluids or for irregular, amorphous solid substances. Below the critical temperature  $T_k$ , the full Eq. (5) had to be applied at least in the case of crystalline substances. A difficulty remained insofar as Schrödinger wished to identify  $T_k$  with the melting point of solid crystals, while Eq. (4) provided too low values. In order to establish agreement with experiment, Schrödinger modified Eq. (5) by inserting the expression  $E + (\mu/3)P$  everywhere for  $E + \frac{1}{3}P$ . He obtained the dimensionless parameter  $\mu$  by identifying the new critical temperature,  $T_k^{\text{Schr.}}$ , i.e.,

$$T_k^{\text{Schr.}} = \frac{\mu a}{1 - \mu b} \quad (6)$$

with the experimental melting point of a given crystalline substance, finding  $\mu$  values slightly above unity. He thus concluded that, "the dielectric substances of Debye below the critical temperature are nothing but solid dielectric substances; the solid substances owe the strong binding of their constituents to just this intense self-electrization, which arranges all molecular moments parallel to a far higher degree than can be achieved by a field applied to a fluid; and thus the anisotropic structure exhibited by all real solids is created."<sup>(22)</sup>

The problem of establishing an equation of state for solids, notably on the basis of the kinetic theory of matter, occupied quite a few physicists in the early 1910s, among them Walther Nernst and Eduard Grüneisen in Berlin, Peter Debye and Simon Ratnowsky in Zurich, and Rudolf Ortway in Munich. The solid state theory developed in its early phase more or less on the lines suggested by Grüneisen<sup>(23)</sup> and Debye<sup>(24)</sup> with essential contributions by Max Born.<sup>(25)</sup>

Schrödinger also treated the subject of the dielectric properties of matter in two further publications: one was a 75-page article on "Dielectrics"<sup>(26)</sup> for the *Handbuch der Elektrizität und des Magnetismus*, and the other was a short note on the theory of anomalous electric dispersion.<sup>(27)</sup> Schrödinger's article for the *Handbuch* consisted of one theoretical part (I) and four primarily experimental parts (II–V). In Part I, after a detailed historical introduction to older theories, he discussed Maxwell's theory of dielectrics and then the electron theory of absorption and dispersion of electromagnetic radiation. In Part II, he presented the experimental methods determining the static dielectric constant, and in Part III those of the dynamical dielectric constant (which includes the refraction and absorption index). He devoted Part IV to the changes in the

dielectric constant (occurring with a change in temperature, in the state of the substance, in the pressure, and in the electric field strength), and in Part V he considered the relationship between the dielectric constant and the chemical constitution and composition of the substances. Schrödinger presented the material in a clear and well-organized form; he referred to an enormous amount of literature—i.e., to several hundred papers including his own<sup>(14)</sup>—published up to the end of the year 1912. The article on dielectrics clearly demonstrated the great diligence and skill of the young Schrödinger and established for him a reputation as a writer of reliable review articles.

In his “Note on the Theory of Anomalous Dispersion,”<sup>(27)</sup> submitted in November 1913, Schrödinger discussed a topic which Egon von Schweidler had treated earlier.<sup>(28)</sup> What Schrödinger addressed in 1913 were not the effects treated earlier by Schweidler (which exhibited a certain analogy to ferromagnetism, including the occurrence of a hysteresis); he rather meant the experimental fact that the refractive index of various substances, e.g., water and alcohol, decreases from a rather high value for low frequencies to a value not much different from unity for optical frequencies. In order to explain such behavior, Peter Debye had recently applied his idea of the existence of rigid, constant electric moments in the interior of molecules.<sup>(29)</sup> He had argued qualitatively that an electric field acting on a dielectric substance would align the axis of their permanent electric moments within a short but finite time interval, thus providing a macroscopic electric moment which causes the high dielectric constant observed in a static field; in an alternating field, especially one with rapid oscillations, the molecules would be unable to align, and as a consequence only the bound electrons, and not the permanent dipoles, would contribute to the dispersion phenomena. Schrödinger, in his paper, examined the theories of Drude<sup>(30)</sup> and Debye,<sup>(29)</sup> but he did not suggest an alternative to Debye’s theory; instead, he proposed to investigate experimentally the situation further and to observe the details of the dispersion curves and their temperature dependence.<sup>(31)</sup>

During his years as an assistant, Erwin Schrödinger published two papers in the series “Contributions to the Understanding of Atmospheric Electricity,” which were spread over among many issues of the *Sitzungsberichte* of the Vienna Academy of Sciences. The initiator of the series was Franz Exner, the head of the Institute, who had himself contributed to the study of atmospheric electricity from the 1880s and transformed Vienna into one of the leading centers of research in that field far into the twentieth century.

The research on atmospheric electricity had been raised to a new scientific level by William Thomson, later Lord Kelvin, when—beginning

in 1859—he devised new precision instruments, such as reliable, even portable, electrometers to determine electric charge, and an instrument to measure the electric field. Interest in the problems of atmospheric electricity continued, notably in Great Britain, the United States (where Henry Rowland became involved), Italy, Germany, and in particular Austria. In Austria, Franz Exner would be the first to arrange balloon observations, which proved the existence of *positive* charges in the atmosphere.<sup>(32)</sup> In Wolfenbüttel, Germany, Julius Elster and Hans Geitel did pioneering work on atmospheric electricity and radioactivity. At the same time, in England, especially at Joseph John Thomson's Cavendish Laboratory, measurements of the electrical properties of the atmosphere were also carried out and theoretical ideas were put forward to explain the observed phenomena. However, Vienna still retained its reputation as one of the main centers for research in atmospheric electricity and radioactivity, with Exner's students performing widely appreciated investigations.

In the fall of 1912, a paper of Erwin Schrödinger, entitled "On the Altitude Distribution of Penetrating Atmospheric Radiation—Theory," was communicated to the Vienna Academy of Sciences; in it he presented a detailed theoretical analysis of the problem of penetrating radiation.<sup>(33)</sup> In particular, Schrödinger attempted to throw light on the origin of penetrating radiation, a question "not easily answered, since because of the penetrating power rather distant sources of radiation also may provide noticeable contributions to radiation intensity at a given space point."<sup>(34)</sup> He wrote that hitherto three possible explanations had been suggested for the origin of the penetrating radiation in the atmosphere, but the opinions of the experts disagreed vehemently about the respective weight of the contributions from: "1. The radioactive substances contained in the ground or precipitated onto the surface of the earth; 2. The radioactive substances suspended in the atmosphere; and 3. Hypothetical extraterrestrial sources of radiation."<sup>(34)</sup> While Rutherford's former collaborator Arthur Steward Eve and the American Louis Vessot King had examined the first contribution,<sup>(35)</sup> Schrödinger now analyzed the second contribution, arguing at the same time that "the third source of radiation is... completely hypothetical, and should be introduced only then with some justification if one should find the other two absolutely insufficient in explaining observations."<sup>(34)</sup> Schrödinger then sought to establish "a calculation, as exact as possible, of the action of radiators suspended in the atmosphere," in order to arrive at conclusions on "the altitude distribution of the radiation substances" and thus also on the "altitude distribution of the [penetrating] radiation."<sup>(36)</sup> This theoretical altitude distribution could then be compared to the data obtained from balloon flights. Schrödinger also discussed the contribution of the usually considered effects of diffusion,

radioactive decay, and gravity to the altitude distribution of penetrating radiation and concluded: "These factors alone would—as a simple calculation shows—just allow the emanations and [radioactive] inductions, originating from ground pores, to ascend to an altitude of a few meters above ground."<sup>(36)</sup>

In August 1913, Schrödinger sought to determine how much Ra A, the first decay product of the so-called radium emanation, was contained in the atmosphere at Seeham and how this amount changed in the course of days and weeks. He performed an extended series of experiments, consisting of "136 single measurements, among them 105 absolute determinations and 91 additional parallel experiments to estimate the mobility of the carriers of Ra A."<sup>(37)</sup> The quantity, which he derived from the measurement, was the so-called "saturation current," i.e., the current maintained by the radioactive precipitation. Schrödinger's experimental work on the Ra A content of the atmosphere constituted more or less an exercise of the type performed in an advanced laboratory course. It provided him with the opportunity to join the active research of his colleagues at Exner's institute and at the *Institut für Radiumforschung*. Thus he confirmed the earlier results of Victor Franz Hess,<sup>(38)</sup> namely "that, even at the time when the Ra A content reaches a maximum, only about a fifth of the total ionization [of the atmosphere] is supplied by the decay products of radium" and "also that the fluctuation of [electrical] conductivity is much greater than can be explained on the fluctuations of radium products alone."<sup>(39)</sup>

Between 1911 and 1914 Friedrich Hasenöhl developed a school of his own at the University of Vienna. Two aspects were remarkable in this context: first, quantum theory finally entered Hasenöhl's institute; and second, the modern theory of solids was taken up and propagated in Vienna. Arthur Haas was the first person in Vienna to make an active contribution to quantum theory with his treatment of the hydrogen atom.<sup>(40)</sup> Although the physicists in Vienna received Haas' ideas with some reservation, the fairly positive judgment about them by the famous Dutch theoretician Hendrik Antoon Lorentz<sup>(41)</sup> made some impression. The first Viennese to respond to Haas' interpretation of Planck's quantum of action by the atomic model was Arthur Schidlof, then at the physical laboratory of the University of Geneva.<sup>(42)</sup> Fritz Hasenöhl himself attacked the problem of obtaining the line spectrum of atoms without referring to a particular model,<sup>(43)</sup> and also encouraged his student Karl Harzfeld to work on an atomic model that would account for the hydrogen spectrum.<sup>(44)</sup> The news about Niels Bohr's theory of the constitution of atoms and molecules reached Vienna during the 85th *Naturforscherversammlung* in September 1913.<sup>(45)</sup> Several months later Karl Herzfeld studied the Zeeman effect, i.e., the splitting of the spectral lines in a magnetic field, in the "two

theories which attempt to use the quantum concept in order to explain the laws of the series spectra, the first by Hasenöhl,<sup>(43)</sup> the second by Bohr<sup>(45), (46)</sup>

Herzfeld belonged to the younger generation of physicists trained by Hasenöhl. Hans Thirring, senior to Herzfeld by four years, had been among his first students. He had studied physics and mathematics at the University of Vienna from 1907 to 1911, receiving his doctorate in 1911; his years as a student at Vienna almost overlapped with those of Schrödinger. Since the fall of 1910, Thirring served as assistant at the theoretical institute of Hasenöhl, supplementing the latter's activities. Thirring contributed actively to problems in theoretical physics. Thus, for instance, he submitted in July 1913 a paper to the *Physikalische Zeitschrift* "On the Theory of Spatial Lattice Vibrations and of the Specific Heats of Solids,"<sup>(47)</sup> by which he opened a new chapter in kinetic and quantum theory in Vienna.

Erwin Madelung had first considered spatial lattices in Göttingen for the purpose of calculating the frequencies of the eigenvibrations of solids from the observed elastic constants.<sup>(48)</sup> Then Max Born and Theodore von Kármán<sup>(25)</sup> studied the theory of spatial lattices in detail; they computed in particular their eigenvalue spectrum by strict mathematical methods, and arrived at an equation for the specific heat of cubic lattices which was very similar to Einstein's,<sup>(49)</sup> namely

$$c_v = 3R \frac{3}{(2\pi)^3} \int_0^{2\pi} \frac{\left(\frac{h\nu_0}{kT}\right) \sin^2\left(\frac{\omega}{2}\right) \exp\left(\frac{h\nu_0}{kT} \sin \frac{\omega}{2}\right)}{\left[\exp\left(\frac{h\nu_0}{kT} \sin \frac{\omega}{2}\right) - 1\right]} \omega^2 d\omega \quad (7)$$

At about the same time, Peter Debye proposed an alternative approach to the theory of specific heats of solids.<sup>(24)</sup> The main difference with the Born-von Kármán theory was that Debye considered the crystal not as an atomic lattice, but as a composite molecule or an elastic continuum, in which  $N$  atoms (in a gram-atom of the substance) performed collective oscillations, and the molecular constitution of the solid only entered into the calculation of the maximum frequency  $\nu_m$ ,<sup>(50)</sup> with the specific heat of the solid being given by<sup>(24)</sup>

$$c_v = \frac{9R}{x_m^3} \int_0^{x_m} \frac{x^4 \exp(x) dx}{[\exp(x) - 1]^2} \quad (8)$$

with

$$x_m = \frac{h\nu_m}{kT} = \frac{\Theta}{T} \quad (8a)$$

$\Theta$  being the characteristic temperature.

For Hans Thirring, a member of the former Boltzmann institute in Vienna, it was of course obvious that the Born-von Kármán atomic-lattice theory had to be preferred above the quasi-continuum approach of Debye. Still he found some point of improvement in Born and von Kármán's work. Born and von Kármán had obtained a general formula for the energy of a cubic solid, namely,

$$E = \frac{RT}{(2\pi)^3} \sum_{k=1} \int \int_0^{2\pi} \int \frac{x_k}{\exp(x_k) - 1} d\phi d\psi d\chi \quad (9)$$

where  $x_k = h\nu_k/kT$  and  $\nu_k$  denote the eigenfrequencies of the spectrum<sup>(51)</sup>; they had then introduced an approximation, by which the threefold integration reduced to a single integration, from which they obtained the expression for the specific heats. Thirring discovered that "this simplifying approximation involves, on the one hand, an assumption which cannot be fully justified; on the other hand, by it the essential feature of Eq. [(9)] is washed out, namely the dependence of the specific heats on the elastic constants of the crystal."<sup>(52)</sup> He therefore attempted to evaluate rigorously the expression (9) of Born and von Kármán, without any doubtful approximation. By making use of the identity

$$\frac{x}{\exp x - 1} = 1 - \frac{x}{2} + \frac{B_2}{2!} x^2 - \frac{B_4}{4!} x^4 + \dots \quad (10)$$

where  $B_i$  denote Bernoulli numbers, and exchanging summations and integrals in the expression for  $E$ , Eq. (9), Thirring eventually found for specific heat the expression

$$c_v = \frac{R}{(2\pi)^3} \int \int_0^{2\pi} \int \left[ 3 - \frac{B_2}{2!} \left( \frac{h}{kT} \right)^2 s_1 + \frac{B_4}{4!} \left( \frac{h}{kT} \right)^4 s_2 - \dots \right] d\phi d\psi d\chi \quad (11)$$

with

$$s_\lambda = (\nu_1^2)^\lambda + (\nu_2^2)^\lambda + (\nu_3^2)^\lambda \quad (11a)$$

For not too small temperatures, i.e.,  $T > (h/k) \sqrt{s_1^{\max}}/2\pi$ , with  $s_1^{\max}$  the largest value of  $s_1$ , the right-hand side of Eq. (11) converged to

$$c_v = 3R \left[ 1 - \frac{B_2}{2!} \left( \frac{h}{kT} \right)^2 I_1 + \frac{B_4}{4!} \left( \frac{h}{kT} \right)^4 I_2 - \dots \right] \quad (12)$$

$$I_k = \frac{1}{3(2\pi)^3} \int \int_0^{2\pi} \int s_k d\phi d\psi d\chi \quad (12a)$$

In this case, all coefficients grew approximately like the  $k$ th power of  $I_1$ , and Eq. (12) coincided with Debye's result, Eq. (8), with  $\Theta$ , the characteristic temperature, now being given by  $\Theta = (h/k) \sqrt{I_1}$ . However, the agreement between lattice theory and continuum theory was not perfect even in this case, because the  $I_k$  depended on the elastic constants of the crystal. When Thirring finally used the known constants for copper, rock-salt, and sylvite and compared the theoretically derived—via Eq. (12)—and the observed specific heats of these materials in the temperature range between  $0^\circ$  and  $80^\circ$  absolute, he found an overall fair description.

Thirring continued to improve on his evaluation of the Born–von Kármán lattice theory. He submitted a detailed paper on the theory to the *Physikalische Zeitschrift*, which was published in two parts.<sup>(53)</sup> With this work he obtained his *Habilitation* at the University of Vienna in 1915. Thirring frequently used to discuss theoretical topics with Schrödinger, who was “mostly the giving partner.”<sup>(54)</sup> This remark also referred to the work on lattice dynamics; indeed Thirring pointed out in his first paper on lattice theory that he had, “following a suggestion of E. Schrödinger,” attempted “to turn the rigorous formula [Eq. (9)] into a [practically] useful expression by expanding it into a series.”<sup>(52)</sup> The two young physicists, in spite of the fact that they belonged to different institutes, clearly took pleasure in discussing problems of mutual interest—the atomic or molecular structure of solids being such a topic—which excited the collaborators of Hasenöhl and Exner alike.

While Thirring worked on an improvement of the theoretical formula for the specific heat of solids, Schrödinger chose to study a primarily experimental question, namely whether the dynamical theory of lattices did account for the observed interference pictures created by the penetration of X-rays through crystals. The discovery of the X-ray interference patterns by Max von Laue, Walter Friedrich, and Paul Knipping in the spring of 1912<sup>(55)</sup> had been a sensation in the scientific world, extending far beyond physics. The interpretation given to the observed effect, namely that it represented the diffraction of electromagnetic radiation of very short wavelengths from the spatial gratings formed by the atoms in the crystals, had solved two problems at the same time: it demonstrated beyond doubt the electromagnetic wave nature of Wilhelm Conrad Röntgen's X-rays; and it proved the atomic lattice structure of crystals.

The observed interference patterns of Friedrich and Knipping exhibited several peculiar features which demanded a theoretical explanation. Especially, the intensity maxima on the film were not more or less circular spots—as had been expected—but rather consisted of extended strokes perpendicular to the direction, connecting the point of the crystal

which was hit by the primary X-rays to the position of the maxima. Von Laue and his student Frank Tank investigated this problem at the University of Zurich and concluded: "For the interference theory of the phenomena occurring when crystals are penetrated by X-rays, the only really important difficulty consists in estimating the role that one should attribute to the influence exerted on it by the heat motion [of the atoms in the crystal]."<sup>(56)</sup> Von Laue also tried to investigate Planck's suggestion that perhaps considerable parts of the space lattice perform nearly the same vibrations, as far as amplitude and phase were concerned; if this suggestion was correct, then the heat motion should reduce the size of the crystal domain acting uniformly; especially since the elongation of the individual spots in the Laue diagram depended on the size of the crystal domain contributing to them, for low temperatures the elongations had to be observed "for those distances [of the crystal] from the anti-cathode for which they cannot be seen anymore in the usual temperatures."<sup>(57)</sup> A later quantitative calculation of the situation by von Laue, however, did not seem to confirm Planck's ideas and the consequences following from them.<sup>(58)</sup>

In deriving these results, von Laue referred to previous work of Peter Debye in Utrecht. In two papers, entitled "On the Influence of the Heat Motion on the Interference Phenomena with X-rays" and "On the Intensity Distribution in the Interference Pictures Created with X-rays," Debye had treated the problem of detailed intensity distribution in the X-ray interference patterns. This investigation had interested Debye not only as providing a contribution to the theory of Laue patterns, but also to the quantum mechanical problem of zero-point energy. In his first paper, Debye simplified the three-dimensional problem considerably: He assumed a linear lattice of points and then calculated the intensity of the scattered X-rays on the assumption that the thermal motions of the electrons in the  $x$ -direction are statistically independent of each other and  $N$  lattice points contribute to the interference picture; he thus arrived at a formula for the averaged intensity at a point  $r$ . In his second paper, Debye extended his previous treatment to the situation of the three-dimensional lattice. In a third, long paper, submitted in October 1913 to the *Annalen der Physik* and published in the first issue of 1914, Debye removed the restriction concerning the mutual independence of atomic vibrations; he assumed, in particular, collective oscillations of the crystal having frequencies which run through all values in the elastic spectrum of the body, thus applying a method which had already proved to be successful in the theory of the specific heats.<sup>(59)</sup>

A few weeks after Debye submitted the above-mentioned paper, Erwin Schrödinger sent his first note on the same topic, entitled "On the Sharpness of the Interference Pictures Created by X-rays," to the



*Physikalische Zeitschrift*, but it appeared a couple of weeks before Debye's paper.<sup>(60)</sup> Schrödinger based his treatment exclusively on the dynamical lattice model of Born and von Kármán, which seemed to him to represent "the most suitable [model] in order to estimate the probable influence of the heat motion on the interference phenomena, obtained by the action of X-radiation on regular crystals."<sup>(61)</sup> In his note, Schrödinger followed—with respect to computational steps—to a large extent the procedure which Debye had taken several months earlier. In particular, he began by treating a one-dimensional atomic lattice with one-dimensional heat motion, since the three-dimensional problem presented rather serious mathematical difficulties if one dropped the assumption of mutually independent atomic vibrations. By making use of the assumptions which Debye had made earlier, namely that the electronic oscillations in atoms were fast in comparison with the atomic period (hence one could average the phases of atomic motion), Schrödinger found that the averaged X-ray intensity  $J$  emitted by the  $N$  atoms of a linear lattice was given by a double sum over the atoms in an exponential—corresponding to the amplitude of the secondary radiation emitted by a single atom multiplied by a Boltzmann factor (denoting the probability of the atoms to assume deviations from their rest positions) and integrated over all possible deviations,  $\xi_1, \dots, \xi_N$ , i.e.,

$$J = \text{const} \sum_m \sum_n \exp[i\omega a(n-m)\theta] \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \exp \left[ -\frac{f}{2kT} \sum_l (\xi_{l+1} - \xi_l)^2 + i\omega \cos \theta (\xi_n - \xi_m) \right] d\xi_1, \dots, d\xi_N \quad (13)$$

where  $\theta$  denotes the angle between the lattice line and the direction from the center of the lattice to the observation point,  $f$  the force constant of the atomic lattice, and  $\omega = 2\pi/\lambda$  ( $\lambda$  being the wavelength of the secondary X-rays). To evaluate the integrals in Eq. (13), Schrödinger introduced—like Born and von Kármán—normal coordinates for the displacement coordinates  $\xi_n$ . Thus he finally found

$$J = \sum_m \sum_n \exp \left[ i\omega a(n-m) \cos \theta - \frac{kT}{2f} \omega^2 \cos^2 \theta \sum_l \frac{(\alpha_{nl} - \alpha_{ml})^2}{p_l} \right] \quad (14)$$

where  $\alpha_{nl}$  denote the coefficients of the transformation matrix and  $p_l$  the momentum variables connected with the eigenfrequencies  $\nu_l$  of the linear lattice by the equation

$$p_l = \frac{m}{f} \nu_l^2 \quad (15)$$

$m$  being the mass of the lattice atoms. Schrödinger computed the sum  $\sum_l (\alpha_{nl} - \alpha_{ml})^2 / p_l$  in the limit of an infinite point lattice as  $|n - m|$ . Then he carried out the remaining double sum over the indices  $n$  and  $m$ , and finally arrived at his intensity formula. He demonstrated that in the vicinity of the intensity maxima, i.e., for  $\alpha = \omega a \cos \theta = 2n\pi + \mathcal{E}z$ ,  $\mathcal{E} = (kT/f) \omega^2 (\cos^2 \theta/2)$ , and with integral  $n$  and  $\mathcal{E} \ll 1$ , the intensity was given by the formula

$$J = 2 \frac{N}{\mathcal{E}} \frac{1}{1 + z^2} \quad (16)$$

From this equation, Schrödinger concluded:

1. With rising temperature, the interference pictures [patterns] become increasingly wide and smeared out in an approximately symmetrical manner. Their width, given by the condition that the intensity of the interference picture drops at its rim to 1% of the central maximum intensity, is proportional to absolute temperature.
2. The central intensity of an interference picture is, according to [Eq. (16)], inversely proportional to  $\mathcal{E}$ , i.e., it is inversely proportional to the absolute temperature.
3. The total radiation intensity contributing to an interference picture [i.e., to the interference spots associated with a given order] does not depend on the temperature.<sup>(62)</sup>

Finally, for large values of  $\mathcal{E}$ , Schrödinger found “a uniform brightening of considerably lower intensity than the original one in the maxima [namely  $N^2$ ], which were *unperturbed* [by the heat motion].”<sup>(62)</sup> He claimed: “There can, however, be hardly any doubt that the laws established so far will also be valid for the three-dimensional case, though only for high enough temperatures, since we have calculated the probability of a given configuration according to the laws of statistical mechanics without taking into account the quantum theory.”<sup>(63)</sup>

On April 4, 1914 Schrödinger submitted a paper “On the theory of the Debye Effect” to *Physikalische Zeitschrift*.<sup>(64)</sup> He pointed out that the summation in Eq. (14) did depend on the boundary conditions chosen at the ends of the linear lattice, since the “normed eigenfunctions”  $\alpha_{nl}$  did so; however, the final result for  $J$  would nevertheless remain untouched by this, provided the number of atoms is sufficiently large; in fact,  $J$  could be evaluated with desirable precision by a simple approximation method which did not depend on boundary conditions.<sup>(65)</sup> Schrödinger considered different boundary conditions, but argued that they would not change the intensity formula (16) either. Encouraged by this success, he went on to

derive further conclusions from his formula (16). He concluded that the "interference phenomenon is caused essentially by the cooperation of relatively close atoms."<sup>(66)</sup> He found that he had substantiated the ideas of Planck, von Laue, and Tank on the origin of X-ray interference phenomena through the synchronous vibrations of large parts of the space lattice, especially the suggestion of von Laue and Tank that the elongation of the interference spots could be reduced by the temperature effect. After clarifying these points of principle, Schrödinger discussed in detail the practical consequences of Eq. (16), describing the intensity of interference spots in the vicinity of maxima. Thus he confirmed again that the total intensity of a spot did not depend on the temperature. He proudly referred to the recent experiments of von Laue and J. Stephan van der Lingen,<sup>(67)</sup> who had observed the disappearance of the interference for a rock-salt crystal at 320°C, as confirming his theory.

For Schrödinger, the main physical problem of the day was still whether one could establish beyond any doubt the atomistic structure of matter and refute decisively the continuum interpretation of matter underlying the so-called phenomenological theories of the properties of matter, which were supported in Austria and elsewhere by the partisans of Mach. The final solution of this problem posed several tasks in physical theory, of which Schrödinger was very much aware. Thus his paper "On the Dynamics of Elastically Coupled Point Systems"<sup>(68)</sup> was very closely related to Boltzmann's views "On the Indispensability of Atomism in Natural Science."<sup>(69)</sup> In Schrödinger's opinion, the atomistic view demanded as a first task that "all those differential equations, which have been obtained by treating a continuous medium by differential equations in the strict sense, must now also be derived... as difference equations on the basis of a model built of molecules."<sup>(70)</sup> He believed that the task "whose solution at first enables one to prove the exclusive validity [of the atomistic view] over the phenomenological theories" had not yet been undertaken.<sup>(71)</sup> It consisted of "finding and predicting *such* conditions, under which the differential equations based on the continuum concept actually lead to observably incorrect results."<sup>(71)</sup> Schrödinger claimed that so far "the only successes in this direction lie in the field of kinetic gas theory,"<sup>(71)</sup> and he mentioned explicitly the temperature jump in the heat conduction and the finite viscosity of rarefied gases as examples of quantities which could be derived from atomistic theory, but not from any phenomenological theory (based on the continuum hypothesis) of heat conduction or internal friction. The discussion of other phenomena on the basis of the atomistic view required dealing with the dynamics of a mechanical system of an enormous number of degrees of freedom, a more or less impossible task. In order to handle this principal difficulty,

Schrödinger now proposed a new integration method for "a system of mass points, which provides in the limit the partial differential equation of the vibrating string, the one-dimensional wave equation."<sup>(72)</sup>

Schrödinger selected the one-dimensional point lattice, not only because of his familiarity with the problem, but also because of the physical importance that it had assumed so far in the theory of specific heats of solids and in the discussion on the influence of temperature on the Laue interference spots. He went back to the equations of a point lattice, in which he assumed that only the nearest neighbors on each side of a given mass point (index  $n$ , mass  $m$ ) exert forces on it, the latter being proportional to the difference between the deviations from the equilibrium positions of the respective mass points; the equations of motion could be brought into the form

$$\frac{dx_n}{dt} = \frac{v}{2} (x_{n+1} - x_{n-1}), \quad n \text{ integer} \quad (17)$$

Schrödinger recognized Eq. (17) as, apart from the factor  $v = [2\sqrt{f/m}]$ , "one of the two fundamental functional relations between three Bessel functions, which lie in a sequence having the fundamental parameter difference of unity."<sup>(73)</sup> Consequently he wrote the solution of Eq. (17) in the form

$$x_n = \sum_{k=-\infty}^{+\infty} x_k^0 J_{n-k}(vt), \quad n = -\infty, \dots, +\infty \quad (18)$$

where  $x_n^0$  denotes the value of  $x_n$  at the time of origin. In the following discussion, Schrödinger showed how the existence of atomic structure accounted for the propagation of energy through the vibrating medium, which is slow compared to the velocity of sound. In a further paper "On the Dynamics of an Elastic Point Sequence," he discussed the case of a linear point lattice, on each of whose mass points acted a time-dependent force; again he gave further applications of his method of solution.<sup>(74)</sup> For Schrödinger these investigations and results seemed to open up a large field for further studies in the kinetic theory of solids for years to come.

The 85th *Naturforscherversammlung* took place in Vienna from September 21 to 28, 1913. This congress was made memorable by the presence of Albert Einstein, who on September 23 spoke on "The Present Status of the Problem of Gravitation."<sup>(75)</sup> The Viennese public had not yet had the opportunity to hear this already very famous scientist, who had discovered special relativity and made fundamental contributions to molecular and quantum theory. He now was attempting to construct a new relativity theory of gravitation, a theory on which he had begun to work actively in

Prague more than two years earlier. Later on, in Zurich, he had developed with Marcel Grossmann, his friend and colleague at the E.T.H., the mathematical formulation of a theory of generalized relativity and gravitation, using the methods of invariant theory and the absolute differential calculus of Elwin Bruno Christoffel, Curbastro Gregorio Ricci, and Tullio Levi-Civita.<sup>(76)</sup> It was on this work that Einstein reported at the Vienna *Naturforscherversammlung*. Einstein's lecture left a lasting impression on the Viennese physicists. It encouraged Friedrich Kottler, Hans Thirring, Ludwig Flamm, and, later, Wolfgang Pauli, to contribute to questions of detail in general relativity theory. Erwin Schrödinger also became deeply involved in Einstein's theory. Indeed, the Vienna *Naturforscherversammlung* stimulated a lot of his future work. This refers as much to his investigations on X-ray interference patterns—which we have already discussed—as to studies in relativity theory, undertaken between 1916 and 1918, and even physiology of vision, which he undertook as late as 1924.

#### 4. SCHRÖDINGER AS *PRIVATDOZENT* AND SCIENTIFIC WORK DURING WORLD WAR I

On January 9, 1914 Erwin Schrödinger joined the illustrious circle of academic teachers at the University of Vienna by obtaining the *Habilitation* in physics. In the following summer semester he taught a course on a topic connected with his own research, i.e., on the “Interference Phenomenon of X-rays,” demonstrating his willingness to teach and propagate the most recent results in physics.<sup>(77)</sup> At the time when Schrödinger received his *Habilitation*, it was by no means clear that he would develop to become a representative of pure theoretical physics. His scientific work covered a wide range of topics, extending from experimental investigations (such as those on atmospheric electricity and radioactivity) to theoretical descriptions of experimental phenomena (such as those on penetrating radiation and X-ray interference patterns) and to genuinely theoretical problems (such as the dynamics of point lattices). It appears that the young Schrödinger had not yet decided on his particular path or rather preferred to become a nonspecialized scientist like his teacher Franz Exner, who had treated both experimental and theoretical topics. In any case, Schrödinger's teaching duties were not restricted to either field, and he announced topics for his courses that reflected this nonspecialization: e.g., in the winter semester of 1914, he gave a course on “Selected Topics of Statistical Mechanics and Quantum Theory,” a topic which was more on the theoretical side.<sup>(78)</sup> His research program in 1914 embraced not only

theoretical work, which we have already discussed, but also purely experimental studies. The programs which required greater experimental skill he performed together with his friend Kohlrausch; others he did completely on his own. Thus, on July 2, 1914, Kohlrausch and Schrödinger communicated to the Vienna Academy of Sciences a paper "On the Soft  $\beta$ -Secondary Radiation from  $\gamma$ -rays."<sup>(79)</sup>

The study of the properties of soft  $\beta$ -radiation created by  $\gamma$ -rays on given materials (metals) provided a fine example of the careful work performed at the *Institut für Radiumforschung* in Vienna. We may assume—in agreement with Schrödinger's confession that, "I learned... in close collaboration with my friend K. W. F. Kohlrausch what experimenting is, without, however, learning it by myself"<sup>(80)</sup>—that Kohlrausch was the leading person in devising the details of the apparatus, while Schrödinger carried out the theoretical calculation, which indeed was very elaborate and made use of results previously obtained by him.<sup>(33)</sup> In spite of this division of work between the two of them, we must not assume that Schrödinger's interests centered at that time purely on theory. Thus, for example, he started in July 1914 an experimental investigation with the goal of studying a special method of determining the capillary constant of fluids. By carefully taking into account all physical processes involved when the bubble of gas leaves the capillary tube, he obtained a new formula. The relation contained a term taking into account second-order corrections in the radius of the capillary tube. He checked his new term by some experiments with extremely wide capillary tubes and registered quite satisfactory quantitative agreement. He submitted the paper, a "Note on the Capillary Pressure in Gas Bubbles," in late October 1914 to *Annalen der Physik*.<sup>(81)</sup> The place from where he submitted the paper—he mentioned Raibl in Carinthia—was where he performed military duties after the outbreak of World War I.

Like so many of his colleagues, Schrödinger was immediately drafted at the beginning of the war in August 1914. In an autobiographical sketch he recalled simply: "Then came the war, in which I participated as an artillery officer at the southeastern front, without getting wounded and without illness and with little distinction."<sup>(80)</sup> He was stationed in several places, first in Raibl (now in Italy), and later in the Hungarian Danube port of Komárom. Later places included Prosecco and the region of Trieste. During the second half of the war, Schrödinger occupied a much less dangerous post than before. Although still on military duty, he spent his time essentially at home. We do not know exactly when he returned to Vienna, but it was certainly before the summer of 1917. In his *curriculum vitae* (of July 1938) he simply remarked that he "later [in the war] was active as a teacher of meteorology."<sup>(82)</sup> Schrödinger's recollection is confir-

med by the existence of a notebook, entitled "Lectures on Meteorology at the Fl[ak]-O[ffiziers]-Schule in Wiener Neustadt," a town lying about 30 km south of Vienna.<sup>(83)</sup> Schrödinger's meteorological lectures to the students attending the military school in Wiener Neustadt did not cover much material beyond that presented in any introductory course on meteorology at the University of Vienna or elsewhere. However, the preparation and delivery of this course led him to continue his former scientific activity, the absence of which he deplored so much while he was stationed at the battlefield. A paper "On the Acoustics of the Atmosphere," which was written in summer 1916 and received by the *Physikalische Zeitschrift* on July 31, 1917, bears the first fruits of his renewed involvement in physical problems, although the essential idea was conceived before Schrödinger returned to Vienna.<sup>(84)</sup> In this paper Schrödinger treated the problem of recognizing the position of explosions, a problem which had been of interest to him as an artillery officer.

Some of Schrödinger's papers during the war represented small contributions, such as the first one, "Note on the Capillary Pressure in Gas Bubbles,"<sup>(81)</sup> or the two short contributions on General Relativity Theory published in early 1918.<sup>(85,86)</sup> Schrödinger also contributed two papers, both on the problem of specific heats,<sup>(87,88)</sup> in which he mainly reviewed the work of others. However, Schrödinger was among those scientists who published only a part of their results, while dealing in private notes with a variety of further questions and problems. This is confirmed by the existence of several notebooks and memoranda, which he wrote during World War I and later kept in his possession. Thus, for example, in his *Nachlaß* there exist notebooks on general relativity theory, on problems of statistical mechanics, and several shorter notes on special theoretical topics.

Foremost among the problems which Schrödinger treated, in his unpublished notebooks and notes, was that of fluctuations. He had probably inherited his interest in those phenomena from his teacher Egon von Schweidler. In late 1914, Schrödinger composed the text of a notebook, entitled "Fluctuation Opalescence," in which he concerned himself with the most important papers on the optical consequences of fluctuations, especially those of Lord Rayleigh, Marian von Smoluchowski, and Albert Einstein.<sup>(89)</sup> Schrödinger emphasized the intimate connection between the optical phenomena and the deviation of the system (exhibiting the optical phenomena) from the dynamical equilibrium. After Smoluchowski's untimely death on September 5, 1917, Schrödinger filled two notebooks on a "Review of the Last Papers of Smoluchowski," analyzing not only the work of the deceased but also showing in detail its relation to the work of Ludwig Boltzmann.<sup>(90)</sup> Schrödinger was greatly inspired by Smoluchowski's work on the consequences of the kinetic theory

of matter. Like Smoluchowski, Schrödinger not only sought to derive subtle formulas, but also studied, immediately afterwards, whether the results did describe the fine details of experimental data. The papers that Schrödinger published on fluctuation phenomena between 1915 and 1919, provide excellent examples of this fact. These papers dealt, respectively, with the "Theory of the Fall- and Rise-Experiments with Particles Exhibiting Brownian Motion,"<sup>(91)</sup> "Note on the Ordering of Chance Sequences,"<sup>(92)</sup> the "Fokker-Planck Theorem,"<sup>(93)</sup> and "Probability-Theoretical Investigations Concerning Schweidler's Fluctuations, Especially the Theory of the Experimental Method."<sup>(94)</sup> With these papers, Schrödinger earned considerable merit as an heir to the great Viennese tradition in kinetic theory, established by Joseph Loschmidt and Ludwig Boltzmann and continued so brilliantly by Marian von Smoluchowski.

Schrödinger took great interest in the principal mathematical method used in Einstein's general relativity theory, namely, the tensor calculus. Thus he developed a systematic approach to mechanics within the framework of general relativity in three (unpublished) notebooks, entitled "Tensor-Analytical Mechanics, I, II, III."<sup>(95)</sup> The ideas of Heinrich Hertz played an important role in Schrödinger's presentation of tensor-analytical mechanics, ideas which Hertz had developed in *Prinzipien der Mechanik*,<sup>(96)</sup> especially his analysis of the fundamental concepts. Hertzian mechanics represented, as the Viennese physicist Franz Paulus stated in 1916, "a certain conclusion of theoretical mechanics, which attempts to eliminate from theoretical mechanics the concept of force as that fundamental, 'not further explainable,' concept, which is associated with unavoidable uncertainties due to the metaphysical connotation."<sup>(97)</sup> General relativity now seemed to dissolve in some way the perhaps most fundamental force in nature, gravitation; hence one could imagine the existence of a deeper relation between Einstein's recent and Hertz' old ideas. With this in mind, Schrödinger composed in 1918 a manuscript, entitled "Hertzian Mechanics and Einsteinian Gravitation Theory."<sup>(98)</sup> The notebooks on "Tensor-Analytical Mechanics" and "Hertzian Mechanics and Einsteinian Gravitation Theory" would play a central role in Schrödinger's invention of wave mechanics in early 1926.

After his return to Vienna from the war, Schrödinger also systematically studied the recent publications on quantum theory, notably those of Max Planck, Albert Einstein, and Karl Schwarzschild. However, he did not immediately become an active contributor to the field of atomic and molecular structure. He began slowly to think about his own way of handling certain fundamental questions arising from it. In the summer of 1919 Schrödinger stated: "A series of theoretical considerations support the opinion that we should think of the emission of light as perhaps a process



composed of *directed* elementary processes, i.e., in such a way that for each emission process radiation goes only into a small, eventually very small, angle of space.”<sup>(99)</sup> If the light-quantum hypothesis gave the correct picture of the nature of light, then two rays of light emerging from a given point of the nature of light source should not interfere when emitted under a large angle. Schrödinger reported the experiment in a paper, “On the Coherence in Wide-Angle Bundles,” which was received by *Annalen der Physik* in August 1919 and published in early 1920.<sup>(99)</sup> The experiment revealed the coherence of different rays, in spite of their wide-angle separation. However, Schrödinger concluded that the result did not contradict the light-quantum hypothesis for the emission process.

This experiment was the last which Schrödinger performed in Vienna and also—apart from a simple investigation in physiological optics<sup>(100)</sup>—the last experiment of the physicist Schrödinger ever. After staying about six months longer at the *II. Physikalisches Institut*, he left Vienna in 1920 to accept the position of an assistant to Max Wien at the University of Jena. The Austrian capital—after the complete defeat of the Austro-Hungarian Empire and its dissolution into a series of independent countries—no longer offered a suitable position. Schrödinger hoped to promote his future scientific career elsewhere. Thus this chapter of Schrödinger’s early life in Vienna ended; he would not return to his hometown and the University of Vienna (apart from short visits) for another thirty-six years.

## 5. FROM VIENNA TO ZURICH

In the spring of 1920, Erwin Schrödinger set out on his way to scientific fame, which led him abroad first to Jena, Stuttgart, and Breslau, then to Zurich and finally to Berlin. Schrödinger was perfectly happy when Max Wien, needing “an assistant for his laboratory courses, who knew enough about modern theories to lecture on them,”<sup>(80)</sup> invited him to his institute at the University of Jena. In April 1920, being newly married to Annemarie Bertel—his Salzburg friend from 1913—he moved to Germany and acquired a *Habilitation* in Jena. Although he was promoted in September of the same year to the personal title (i.e., a nonstaff position) of an extraordinary (i.e., associate) professor, he decided to move to the *Technische Hochschule* in Stuttgart as *Extraordinarius* for theoretical physics. Even Stuttgart was not able to keep Schrödinger for longer than the winter semester of 1920/1921, and he moved on in the spring of 1921 to the University of Breslau as an *Ordinarius* (i.e., full professor). Then the offer from the University of Zurich reached him, and he was appointed professor of theoretical physics on October 15, 1921. He would spend nearly six years

in Zurich, a busy, flourishing, and peaceful city, which was so different from the overcrowded post-war Vienna. In spite of the fact that Zurich lacked the greatness of the imperial tradition, it provided Schrödinger with a stable background, giving him the time necessary to pursue his own scientific work, far from any hectic activity, which he disliked. As a consequence, Schrödinger settled down and was able to make a discovery that established his reputation as one of the greatest physicists of the twentieth century.

Being provided with the necessary security and leisure at Zurich, Schrödinger fulfilled his teaching duties at the university, presenting several courses each semester in addition to holding seminars and tutorials (*Proseminars*) in theoretical physics for less advanced students. Between 1922 and early 1926 he contributed eighteen papers and elaborated on two extended review articles. As in the Vienna period, Schrödinger did not devote himself to one or even a few topics, but treated, simultaneously, a variety of problems in theoretical physics; thus he wrote four papers on atomic structure, three papers plus a handbook article on the quantum theory of specific heats, six papers on gas statistics, four papers plus a review article on color vision and color theory, and one paper on relativity theory. If one examines these papers on diverse topics, one finds that Schrödinger did indeed concentrate on one major field more than any other, namely kinetic theory and the modifications introduced in it by the requirements of quantum theory. If one adds to this the papers on gas statistics and on the specific heats of solids and gases, then they represent half of all publications of Schrödinger in that period. The emphasis on statistical problems is deepened if one adds to the published papers the many extended notes and notebooks, which Schrödinger worked out during the same period and which dealt in some detail with the problems of classical molecular statistics, degeneracy, and quantum statistics. Hence it is no exaggeration to claim that Schrödinger developed, in the four years between 1922 and the end of 1925, a systematic research program on quantum statistical mechanics—a research program, which would then pass smoothly into another program, that of establishing the theory of wave mechanics.

## 6. PROBLEMS OF ATOMIC STRUCTURE

While the concern with problems of kinetic theory and quantum statistics must be considered to be the natural continuation of his earlier research, the interest in problems of atomic structure meant a novel feature in Schrödinger's scientific work. This interest was certainly enhanced by his

leaving Vienna in 1920, since questions of the inner constitution of atoms and molecules had been neglected so far in the official physics community over there. The situation was totally different in those places in Germany where Schrödinger moved to in 1920 and 1921; in Jena, as well as in Stuttgart and Breslau, there were colleagues who were enthusiastic about the latest results obtained from quantum theory, and in particular its application to atomic and molecular structure, yielding an explanation of the observed spectra. Certainly Arnold Sommerfeld's popular and famous book *Atombau und Spektrallinien* of 1919 had contributed greatly to this situation. Schrödinger became personally acquainted with Sommerfeld in the fall of 1919, when he visited Munich and delivered a talk on needle radiation in the *Kolloquium*. There he also met Wolfgang Pauli, his younger fellow countryman, who studied with Sommerfeld at that time. Pauli and Schrödinger established a friendship and exchange of ideas orally and by written communications, which would last to the end of their lives.

Schrödinger's first communication on the theory of atomic spectra dealt with an attempt at a model-like interpretation of the terms of the sharp subordinate series, especially in the case of the alkali spectra, and was submitted in January 1921 to *Zeitschrift für Physik*, where it was published a few weeks later.<sup>(101)</sup> It had been thought that the mutual interactions of the electrons caused perturbations of the series electrons in all atoms except the hydrogen atom.<sup>(102)</sup> However, as Schrödinger noted: "The nature of the perturbation is not known, but it must be considerable; the orbit [of the series electron] cannot, even in an approximation, be a *Keplerian ellipse*."<sup>(103)</sup> Schrödinger proposed that the perturbation arose from the fact that the orbit of the series electron closely approaches the inner electron shell. In order to evaluate quantitatively the perturbation of the orbit of the series electron, Schrödinger neglected the deformation of the inner shell caused by the impinging outer electron, and replaced the action of the inner shell on the electron by that of a sphere, on whose surface the charge is uniformly distributed. Then the orbit of the series electron could be separated into two pieces: an outer one—i.e., lying outside the inner shell—created by the attraction of a unit charge, and an inner one, created by the attraction of an effective charge that was—in the case of sodium—nine times as big. Evidently, the curvature of the inner elliptic orbit was much larger than that of the outer. By applying standard Bohr-Sommerfeld theory to both pieces in a straightforward way, Schrödinger obtained the following expression for the energy term of the series electron:

$$W = -\frac{Z^2 e^2}{2a_0} \frac{1}{(n^*)^2} \quad (19)$$

In Eq. (19),  $Ze$  denotes the nuclear charge in the interior of the inner shell—Schrödinger took, in the case of sodium, the total nuclear charge;  $a_0$  is the radius of the first Bohr hydrogen orbit, and  $n^*$  represented an effective total quantum number, which assumed in Schrödinger's calculation the values

$$n^* = 1.26, 2.26, 3.26, \dots \quad (19a)$$

He concluded: "The suspicion that this type of orbit is associated with the  $s$ -term, therefore, is very suggestive."<sup>(104)</sup>

Schrödinger's work on the sharp subordinate term of alkali atoms emerged from a simple physical idea and helped to remove a principal difficulty in the existing Bohr–Sommerfeld theory. By applying simple mathematical methods—which resembled those which he had employed nine years earlier in his paper on the contribution of metallic conduction electrons to magnetism<sup>(12)</sup>—Schrödinger had obtained a valuable result for the interpretation of atomic spectra. Niels Bohr took favorable note of Schrödinger's paper on the  $s$ -terms of alkali atoms on several occasions.<sup>(105)</sup>

In early October 1922, Schrödinger submitted a paper to *Zeitschrift für Physik* "On a Notable Property of Quantum Orbits of a Single Electron."<sup>(106)</sup> In a letter to Schrödinger, written around December 10, 1926, Fritz London—a few months before he went to join Schrödinger in Zurich—claimed that this paper contained the essential, if not decisive, ideas of undulatory mechanics, which Schrödinger would introduce more than three years later. London even jokingly implied that Schrödinger, "like a priest," had in 1922 kept his results "a secret" from his contemporaries.<sup>(107)</sup> The first hint on the subject of the paper may be found in a letter which Schrödinger wrote to Pauli early in November 1921, shortly after he arrived in Zurich. Pauli had sent him a copy of his review article on relativity,<sup>(108)</sup> and Schrödinger wanted to thank him for it. After thanking him, Schrödinger asked the question: "Are electron orbits geodetic lines or not?"<sup>(109)</sup> Schrödinger went on to argue that the answer should be "No." "Because," he wrote, "if I put into the field of a charged, massive [atomic] nucleus an electron and a neutral mass point at the same point in the same direction and with the same initial velocity, then they exhibit totally different motions."<sup>(109)</sup> Hence, he concluded, the law for a geodetic line did not in reality play a fundamental role, as in nature non-charged smallest particles do not exist. The question asked by Schrödinger seemed to be very simple, and his answer certainly satisfied Pauli as much as the additional remark: "The law [of the geodetic line] just applies approximately to the center-of-mass motion of the larger, on the whole noncharged, systems in fields and on orbits, such that the dimensions of the system can be neglected as being too small."<sup>(109)</sup> However, what law then

replaced the law for the geodetic line of general relativity theory in the case of the inner motions of electrons in an atom? Schrödinger tried to answer this question in his paper of October 1922 on the notable property of the single electron orbits.

From his attempt at a unified theory of gravitation and electromagnetism, Hermann Weyl had attempted to derive particular solutions describing a spherical electron and its motion,<sup>(110)</sup> and he summarized both the successes and the difficulties of this approach in the later editions of his book *Raum-Zeit-Materie*.<sup>(111)</sup> In particular, he discussed the hypothesis of Bohr's quantum theory of atomic constitution, according to which electrons circulating in individual stationary states should not emit radiation. He concluded "Our field equations make assertions only about *the possible states of the field*, and *not about the conditioning of the states of the field by the matter*. This gap is filled by the *quantum theory* in a manner in which the underlying principle is not yet fully grasped."<sup>(112)</sup> More than a year later Schrödinger claimed that he might have found a key to close this gap.

Schrödinger was fairly well acquainted with the geometrical methods of Hermann Weyl. In Weyl's geometry, the linear form  $\phi_i dx_i$  ( $=\phi_0 dx_0 + \phi_1 dx_1 + \phi_2 dx_2 + \phi_3 dx_3$ ), which determined the change of the measure  $l$  of a distance (*Strecke*) in what he called "congruent transference"<sup>(113)</sup> through the equation

$$dl = -l\phi_i dx_i \quad (20)$$

also described the electromagnetic field. Schrödinger started out from the integrated form of Eq. (20) for the transference or the displacement of the measure  $l$ ,

$$l_{P'} = l_P \exp \left\{ - \int_P^{P'} \phi_i dx_i \right\} \quad (21)$$

expressing  $l$  at point  $P'$  in terms of its value at point  $P$ , and an exponential factor containing a path integral (extending from  $P$  to  $P'$ ) over the linear form  $\phi_i dx_i$ . By introducing explicitly the usual electromagnetic potentials, i.e., the Coulomb potential  $V$  and the axial vector potential  $\mathbf{A}$  ( $=A_x, A_y, A_z$ ), as

$$\begin{aligned} \phi_0 &= \gamma^{-1} eV, & \phi_1 &= -\gamma^{-1} \frac{e}{c} A_x \\ \phi_2 &= -\gamma^{-1} \frac{e}{c} A_y, & \phi_3 &= -\gamma^{-1} \frac{e}{c} A_z \end{aligned} \quad (22)$$

where  $\gamma$  denotes a universal proportionality constant yet to be determined,

the exponential factor on the right-hand side of Eq. (21) could be written in the form

$$\exp \left\{ - \int_p^{p'} \phi_i dx_i \right\} = \exp \left\{ - \frac{e}{\gamma} \int_p^{p'} (V dt - A_x dx - A_y dy - A_z dz) \right\} \quad (23)$$

Schrödinger then claimed: "The property of the electron orbits which appears notable to me, as announced in the title [of the paper], is the following: the 'true' quantum conditions, i.e., those which suffice to fix the energy and therefore also the spectrum [of the atom], are also just sufficient to turn the exponent of the distance factor [(23)] into an integral multiple of  $\gamma^{-1}h$  for all approximate periods of the systems."<sup>(113)</sup>

Schrödinger proved this assertion by considering in detail five examples of electron orbits in atoms, as described by the Bohr-Sommerfeld theory. For example, in the case of a nonperturbed Kepler motion of the electron, he derived from the single quantum condition—i.e., the relation  $2\tau\bar{T} = nh$ , where  $\tau$  denoted the period,  $\bar{T}$  the average kinetic energy of the electron,  $n$  the integral quantum number, and  $h$  Planck's constant—and the relation between the average kinetic energy and average potential energy—i.e.,  $\bar{T} = \frac{1}{2}e\bar{V}$ —the equation

$$e\tau\bar{V} = e \int_0^\tau V dt = nh \quad (24)$$

As a consequence the distance factor, Eq. (23), became in this case  $-nh\gamma^{-1}$  for an entire period  $\tau$ . Schrödinger succeeded in verifying Eq. (24) to be true in all cases of multiply periodic electron orbits. He summarized the results in the following words: "If the electron in its orbit carried along with it a "distance" ("*Strecke*"), which is transferred unchanged during the motion, then the measure of this distance would—if one started from an arbitrary point of the orbit—always be multiplied by an integral multiple of  $\exp\{h/\gamma\}$ , whenever the electron returns approximately to its initial position and simultaneously to its initial state of motion."<sup>(114)</sup> Schrödinger concluded: "It is hard to believe that this result is but an accidental mathematical consequence of the quantum conditions and does not possess any deeper physical meaning."<sup>(115)</sup> Finally, Schrödinger discussed the values which the constant  $\gamma$  might assume, suggesting as possible choices  $h$  and  $e^2/c$ . Taking  $e^2/c$  would yield the very high value of  $\exp(1,000)$  for the exponential factor (23). If, however, he chose for  $\gamma$  the purely imaginary value

$$\gamma = \frac{h}{2\pi\sqrt{-1}} \quad (25)$$

the exponential factor (23) became equal to unity, hence “the measure number of a distance (“*Strecke*”) carried along [by the electron] would be reproduced after each quasi-period.”<sup>(115)</sup>

This is as far as Schrödinger’s considerations extended in the fall of 1922. Had he known more, had he even in mind speculative suggestions on how to give the “notable property” of quantum orbits a suitable interpretation, Schrödinger certainly would not have hesitated to phrase them properly. As it was, Schrödinger’s paper did not stimulate a wider audience; his Viennese colleague Adolf Smekal wrote an extended review of it for the *Physikalische Berichte*.<sup>(116)</sup> In this review Smekal drew attention to an article by William Wilson of London that was published in the *Proceedings of the Royal Society of London*<sup>(117)</sup>; in it Wilson proposed an extension of the quantum conditions in a general relativistic scheme, i.e.,

$$\oint \left( p_k + \frac{e}{c} A_k \right) dq_k = n_k h \quad (26)$$

where  $p_k$ ,  $q_k$ , and  $A_k$  denoted the components of momentum, position, and of the electromagnetic potential, respectively. Smekal pointed out that it was possible to derive Schrödinger’s specific results by applying Eq. (26).<sup>(118)</sup>

In a paper on “Bohr’s Atomic Model and Relativity Theory,”<sup>(119)</sup> Karl Försterling of Königsberg examined the question of the compatibility of the quantum and relativity theories. He stated: “Quantum theory and relativity seem to be occasionally considered as opposing fields, because quantum theory is at variance with Maxwell’s equations, the starting point of relativity theory. Since, however, the principle of relativity claims to be universally valid, quantum theory must nevertheless yield to it.”<sup>(120)</sup> He then demonstrated how Bohr’s frequency postulate, which indeed contradicted classical electrodynamics, fitted smoothly with relativistic invariance, in such a way that the specific line-shifts followed, as predicted by special and general relativity theories. Wolfgang Pauli, in his review of Försterling’s paper in *Physikalische Berichte*, then criticized the derivation given for the transverse Doppler shift of spectral lines by noting: “It should, however, be noted that the transformation formula, used by the author for the emitted energy, is valid only if in [the rest frame of the atom]  $K'$  no momentum is emitted at all.”<sup>(121)</sup> About a year later Schrödinger filled the gap in Försterling’s proof; he published the complete solution of the problem of the Doppler effect within the quantum theory of atomic spectra in a note on “Doppler’s Principle and Bohr’s Frequency Condition,” which he submitted on June 7, 1922 to the *Physikalische Zeitschrift*.<sup>(122)</sup> Schrödinger did not primarily intend, with his note, to establish the Dop-

pler effect in Bohr's theory of atomic structure; Schrödinger came across this problem while systematically studying the theory of molecular spectra. The then available theory took into account three terms contributing to any energy state of a given molecule: first, the electronic term; second, the term arising from the oscillations of the nuclei; and third, the term due to the rotations of the molecule. In 1922, Schrödinger argued that there must exist a fourth translational term, smaller than the others, which does not appear quantized but leads to a finite broadening of all spectral lines.

Schrödinger proceeded to solve the problem in a straightforward way. In the special case of an atom moving in the same direction as the momentum transferred by it to the emitted quantum of radiation, he applied the laws of energy and momentum conservation, i.e.,

$$\Delta v = \frac{1}{h} \left( \frac{m}{2} v_1^2 - \frac{m}{2} v_2^2 \right) \quad (27)$$

and

$$mv_1 = \frac{h\nu}{c} + mv_2 \quad (28)$$

where  $m$  denotes the mass of the atom or molecule, and  $v_1$  and  $v_2$  its velocity before and after the emission of a light-quantum having energy  $h\nu$  and momentum  $h\nu/c$ . On inserting Eq. (28) in Eq. (27), he found the relation

$$\frac{\Delta v}{v} = \frac{v_1 + v_2}{2c} \quad (29)$$

yielding the elementary, classical Doppler effect.

In order to attack the more general situation, Schrödinger first defined the energies of the atomic system in its proper frames of reference before and after the emission of radiation,  $E_1(1 - v_1/c^2)^{-1/2}$  and  $E_2(1 - v_2/c^2)^{-1/2}$ , respectively. Consequently, he wrote Bohr's frequency condition as

$$h\nu = \frac{E_1}{\sqrt{1 - v_1^2/c^2}} - \frac{E_2}{\sqrt{1 - v_2^2/c^2}} \quad (30)$$

For the most general case, in which the initial and final velocity vectors made angles  $\theta_1$  and  $\theta_2$  with the momentum vector of the emitted radiation, momentum conservation then provided the two equations

$$\frac{E_1 v_1 \cos \theta_1}{c^2 \sqrt{1 - v_1^2/c^2}} = \frac{E_2 v_2 \sin \theta_1}{c^2 \sqrt{1 - v_2^2/c^2}} + \frac{h\nu}{c} \quad (31a)$$



and

$$\frac{E_1 v_1 \sin \theta_1}{c^2 \sqrt{1 - v_1^2/c^2}} = \frac{E_2 v_2 \sin \theta_2}{c^2 \sqrt{1 - v_2^2/c^2}} \quad (31b)$$

By combining Eqs. (32) and (33a), (33b), he finally obtained

$$v^* = v \sqrt{\frac{c - v_1 \cos \theta_1}{\sqrt{c^2 - v_1^2}}} \frac{c - v_2 \cos \theta_2}{\sqrt{c^2 - v_2^2}} \quad (32)$$

connecting the frequency  $\nu$  (shifted by the Doppler effect)—the classical plus the relativistic corrections—to the “rest-frame” frequency  $\nu^*$ , defined by

$$\nu^* = \frac{E_1^2 - E_2^2}{2h \sqrt{E_1 E_2}} \quad (32a)$$

Schrödinger's derivation of the full, relativistic Doppler effect for spectral lines emitted by atoms and molecules was immediately recognized as an important contribution to atomic theory. Niels Bohr mentioned it in his review article, “On the Application of Quantum Theory to Atomic Structure. Part I. The Fundamental Postulates,” submitted in November 1922 to *Zeitschrift für Physik*.<sup>(123)</sup>

In a letter to Wolfgang Pauli, dated November 8, 1922, Schrödinger gave a discussion of his treatment of the Doppler effect, which—he admitted—was based entirely on the light-quantum hypothesis and the laws of energy-momentum conservation. He wondered, however: “But the Devil knows whether our atomic systems also change according to *necessity* only, or are determined by *strictly causal laws*, not to mention whether or not they behave like conservative mechanical systems.” He, Schrödinger, believed that the “‘solution’ to the terrible contradictions of quantum theory” had to be sought along the path suggested by Franz Exner, i.e., by assuming an essentially statistical nature of the physical laws, and: “Can it not be imagined that the conservation of energy-momentum is a macroscopically valid average relation, which is unknown to atomic physics in the same way as the second law of thermodynamics? At least, it *may* be that way—and I can see nearly no other way out.”<sup>(124)</sup>

Schrödinger presented his doubts on the validity of energy and momentum conservation, when applied to processes involving a single or a few atoms, in his inaugural address at the University of Zurich delivered on December 9, 1922.<sup>(125)</sup> But he did not apply such ideas in his own research on quantum and atomic theory. However, when in the spring of 1924 Bohr, Kramers, and Slater published their new radiation theory,<sup>(126)</sup>—in which

they enunciated the idea of “statistical” rather than “strict” energy-momentum conservation in atomic processes, Schrödinger reacted quite enthusiastically. Soon thereafter he wrote to Bohr: “I have just read with the greatest interest the fascinating turn of your ideas in the May issue of *Philosophical Magazine*. This turn touches me extremely sympathetically. Being a disciple of the old Franz Exner, I have long since become acquainted with the idea that our statistical laws are probably not based on ‘microscopic’ lawfulness, but perhaps on ‘absolute chance,’ and that perhaps even energy and momentum conservation are only statistically valid.”<sup>(127)</sup> Some time later, Schrödinger composed an extended note on “Bohr’s New Radiation Hypothesis and the Energy Conservation Law,”<sup>(128)</sup> in which he stated that the “new conception... demands equally great interest from the point of view of the physicist and philosopher,” because: “By it the opinion, which has been put forward by several authors, i.e., that the single molecular process might perhaps not be determined uniquely and causally through ‘laws,’ is realized for the first time.”<sup>(129)</sup>

In his note, published in the *Naturwissenschaften* issue of September 5, 1924, Schrödinger first summarized the main features of the Bohr–Kramers–Slater theory: the hypothesis of the virtual radiation field of the atoms, containing the frequencies of all spectral lines emitted by them, with the associated transition probabilities, the validity of energy conservation on the statistical average over many atomic processes; the new approach to the phenomena of dispersion of light by atoms essentially on the basis of the concepts of wave theory; and the explanation of the Compton effect and of the natural line-widths of spectral lines. Then he gave his endorsement to the basic ideas of the Bohr–Kramers–Slater theory by adding a few considerations of his own, in which he attempted to illustrate both the consequences and the origin of statistical energy conservation.

During 1924 and 1925 Schrödinger’s scientific exchange with Pauli remained in abeyance, while he came into closer contact with the latter’s teacher Arnold Sommerfeld. In November 1924 he received, as a present from Sommerfeld, a copy of the new, fourth edition of *Atombau und Spektrallinien*,<sup>(130)</sup> and he at once returned his heartiest and warmest thanks in a letter. Sommerfeld’s book immediately provided a stimulus for Schrödinger’s work, as he remarked in his letter: “On p. 737 I found the *Motto* for a little note, which I was just about to submit, namely on the rotational heat of  $H_2$ , with half-integral quantum numbers for molecular rotation.”<sup>(131)</sup> On April 7, 1925 Schrödinger submitted a paper on “The Hydrogen-like Spectra from the Point of View of the Polarizability of the Atomic Core” to the *Annalen der Physik*, where it appeared in the June issue.<sup>(132)</sup> It complemented Schrödinger’s 1921 paper<sup>(101)</sup> and gave a full

treatment of *all* alkali and alkali-like terms; the former paper had dealt with nonhydrogen-like terms, and the new one dealt with hydrogen-like terms. In his new paper on the alkali spectra and the like, Schrödinger tried to go as far as possible in rescuing the Bohr–Sommerfeld's concepts of atomic structure, as he desired “not to let the light extinguish, which had shone through Sommerfeld's calculation on the structure of the Ritz term formula.”<sup>(133)</sup> He was little bothered by the fact that parts of his analysis were contained in an earlier paper by Douglas Rayner Hartree of Cambridge, which he had overlooked.<sup>(134)</sup> He just knew that he had successfully carried through the idea hinted in Sommerfeld's book, for, as he wrote to Sommerfeld, he had received “an injection of *Münchenin*, otherwise the child would never have been born.”<sup>(135)</sup>

## 7. COLOR VISION AND PHYSIOLOGICAL OPTICS

Color theory is one of the central issues of physiological optics, i.e., the field of optics dealing with the perception of sensation of (mainly) the human eye. Aristotle had treated this question in antiquity, but later interest discontinued in Europe until the seventeenth century. Isaac Newton, with his experimental analysis of light, then provided a physical definition of colors. Newton's identification of color with the physical properties of light stimulated, in the early nineteenth century, harsh criticism of the poet and naturalist Johann Wolfgang von Goethe, who developed a totally different color theory. Goethe's ideas concerning the origin and decomposition of colors did not attract physicists in the following decades. The physiologists of the nineteenth century then classified many aspects of color vision; for example, Johannes Evangelista Purkinje investigated the phenomena of color observation in the dark, discovering the so-called Purkinje effect, i.e., the fact that blue remains perceptible longer as a distinct color than does red when brightness is diminished.

The modern development in color theory started with the English physicist and physician Thomas Young, who not only revived the wave theory of light but also worked on the specific properties of the eye and on color vision. His work was extended by Hermann von Helmholtz, A. Grassmann, James Clerk Maxwell, and Edward Hering. Shortly after 1900, Franz Exner of Vienna wrote a series of papers on the problem of color vision, which was intimately connected with the physiological problem of color sensitivity in the human eye. During the second decade of the twentieth century, A. H. Munsell in Boston and Wilhelm Ostwald in Leipzig developed an organization of the body colors or pigments based on a physiological point of view.<sup>(136)</sup> Ostwald, for example, proposed a color

atlas containing 2500 color points, each determined by a set of three coordinates—the black content, the white content, and the color content.<sup>(136)</sup> Then K. W. Fritz Kohlrausch<sup>(137)</sup> in Vienna severely criticized Ostwald's color theory, but Kohlrausch's complaints against Ostwald were not shared by all physicists. Kohlrausch dismissed the opinions against his own criticism of Ostwald as being founded on inconsistent assumptions.<sup>(138)</sup> The debate for and against Ostwald's color theory continued in the following years.

In early August 1920, an article by Erwin Schrödinger on "Theory of Pigments with the Highest Luminosity" appeared in *Annalen der Physik*.<sup>(139)</sup> By analyzing the shape of the re-emission function—which according to the Vienna school allowed one to define quantitatively the property of brightness of a given color—he demonstrated that a pigment (or body color) under investigation could possess finite, maximum brightness under one condition: the re-emission function assumes for the entire visible spectrum the values 0 and 1 and shows only two discontinuities (i.e., jumps from 0 to 1, and *vice versa*) over the entire range. In this autobiographical note, presented in 1933 to the Nobel Foundation, Schrödinger stated that his "papers on color theory originated from discussions with Kohlrausch and Exner and from reading Helmholtz' publications"<sup>(1)</sup>; indeed, the main stimulus in attacking the difficult problem of defining the property of brightness in a consistent theory came from Helmholtz.

In a series of papers published in 1891, Hermann von Helmholtz had attempted to solve the problem of comparing the brightness of two different colors by "a generalized application of Fechner's law to color theory," using "the shortest lines in the color system," defined in a suitable Riemannian space.<sup>(140)</sup> Helmholtz had prepared these studies by previously analyzing the validity of the so-called Weber–Fechner law in physiology, stating that the sensation of intensity is proportional to the logarithm of the stimulus intensity; he had especially shown that some apparent violations of the law might arise from the characteristic light ("*Eigenlicht*") of the retina.<sup>(141)</sup> With the new confirmation of the Weber–Fechner relation in color perception, Helmholtz then turned to his main task, namely the interpretation of color system—in which each color was given by three independent variables—as a three-dimensional Riemannian manifold. Helmholtz derived an expression for the difference of sensation intensity,  $dE$ , in terms of an admixture of color components,  $dx$ ,  $dy$ ,  $dz$ , to a given color—characterized by the triple numbers  $(x, y, z)$ —namely,

$$dE = \text{const} \sqrt{\left(\frac{dx}{x}\right)^2 + \left(\frac{dy}{y}\right)^2 + \left(\frac{dz}{z}\right)^2} \quad (33)$$

Helmholtz had originally hoped that the line-element—i.e., the expression describing infinitesimal distances in the three-dimensional Riemannian color space—exhibited a particularly simple structure when expressed in terms of fundamental colors; however, he had not been able to achieve this goal. “This fact, and a computational error in Helmholtz’ paper, whose discovery further weakens the connection [of the theory] to experiment, may be cited as the reason why his [Helmholtz’] intellectually interesting idea of a Riemannian geometry of colors has not been appreciated and—so far as I know—has not been followed further,” remarked Schrödinger nearly thirty years later.<sup>(142)</sup> Schrödinger, who had previously become acquainted with Riemannian geometry while working on problems of general relativity theory, now tried to improve Helmholtz’ ideas by developing, in a set of three memoirs, the “basic outlines of a theory of color metric for daylight vision.” He submitted these papers in March 1920 to *Annalen der Physik*, where they were published in November of that year.<sup>(142–144)</sup> At the same time, he presented the main ideas on what he called “color metric” (“*Farbenmetrik*”) in a short note sent to *Zeitschrift für Physik*; this article appeared in June 1920 as Schrödinger’s first publication on color metric.<sup>(145)</sup>

Schrödinger approached the problem of “color geometry” from the strict point of view of an experimentalist, rather than from a physiological or psychological point of view which, for instance, had guided Wilhelm Ostwald. The problem posed in color metric was to find a method of measuring quantitatively all three parameters characterizing a pigment color. Evidently, the solution implied a distinct, objective decision about the equality or inequality of any two given colors. As Helmholtz had stated clearly in 1891, the main difficulty rested in the fact that the color space was three-dimensional. Schrödinger systematically divided the entire task of color metric into two parts. In Part I, which he called the “lower color metric” (“*niedere Farbenmetrik*”), he restricted himself to using only methods that allow one to decide whether two or more given colors are *equal*; in Part II, entitled “higher color metric” (“*höhere Farbenmetrik*”) or “genuine metric of colors” (“*eigentliche Metrik der Farben*”), he applied the method of greatest similarity—which had been suggested earlier by Hermann von Helmholtz. Mathematically different methods had to be used in both cases: for the lower color metric an affine, linear space sufficed, while for the higher color metric a genuine curved Riemannian space proved to be necessary.

Schrödinger devoted two of the three memoirs to displaying the lower color metric. In the first memoir he laid down the definitions and assumptions of standard three-color theory: he defined, for example, the concept “color” as denoting a group of identical looking lights (“*Lichter*”)

having a characteristic spectral distribution function  $f(\lambda)$ —the wavelength  $\lambda$  extending over the visible spectrum between 400 and 800  $\mu\text{m}$ ; he further assumed that the distribution function satisfied the addition and multiplication laws—the so-called Grassmann laws—and reproduced the known results by applying the mathematics of affine spaces.<sup>(142)</sup> In the second memoir he dealt with the specific manifold describing the observed colors, i.e., a kind of cone (having the shape of a paper bag) whose apex coincides with the origin—denoting all colors having zero brightness—and on the base the pure spectral colors red, green, and violet are ordered in their correct sequence in a closed curve, the extreme red and violet being connected by a straight line containing the purple colors, which fill the gap in the physical spectrum as opposed to the physiological spectrum.<sup>(143)</sup> Schrödinger also showed in the same paper how any color could be broken down into a given system of three noncoplanar vectors representing gauge colors and how changing the gauge colors could be achieved by a coordinate transformation in the three-dimensional affine space; and, finally, he discussed the different types of color blindness within the concepts of this theory.

The need to extend the color metric of the affine space, or the lower color metric to the higher color metric, arose from a very simple practical question: How could one divide in the case of two given colors causing different sensations which was the brighter one? Schrödinger noted in his third memoir: “The relation of the lengths of the associated vectors does not primarily decide the case. We may indeed assign to the three colors, the gauge colors, three completely arbitrary vectors, e.g., associate quite a short vector with a very bright color and at the same time a very long vector with a dark color.”<sup>(146)</sup> As a consequence, it was not possible to deduce any information about the magnitude of separation between two colors from the distance between the associated points on or in the color cone. Still, the separation of two colors, including the separation of their respective brightnesses, made sense in human observation. To find an appropriate theoretical description, Schrödinger picked up the earlier idea of Hermann von Helmholtz stating that the use of the Weber–Fechner law—i.e., the law accounting for the intensity of sensations—in the three-dimensional color space demanded the introduction of Riemannian geometry; the shortest connection joining two points representing given colors in this space, obviously invariants in this higher color space, provided a physical measure for the separation of colors.

To determine the properties of the required Riemannian space, Schrödinger stated three necessary assumptions. First, he introduced the quadratic line element  $ds^2$ , i.e.,

$$ds^2 = \sum_{i=1} \sum_{k=1} a_{ik} dx_i dx_k \quad (34)$$

with the coefficients  $a_{ik}$  representing functions of the coordinates  $x_i$  and  $x_k$  ( $i, k = 1, 2, 3$ ) which describe two colors. Second, he assumed that, for two barely separable colors, the  $dx_i$ ,  $dx_k$ , and  $ds^2$  constitute differentials, with  $ds$  having the same value for each color pair. "The *Ansatz* [(34)] completely determines, as is known, a metric for the manifold of numbers of triples  $(x_1 x_2 x_3)$  in the general sense of Bernhard Riemann, if one interprets  $ds$  as the *line element* of this manifold. Hence we are now and only now allowed to speak about a proper metric of color space."<sup>(147)</sup> As the third assumption, he claimed: "The difference between arbitrary colors is judged according to the magnitude of  $\int ds$ , taken for the shortest connecting line (the geodetic line) drawn between the two color points of the manifold, whose measure is given by Eq. [(34)]."<sup>(148)</sup> Schrödinger finally suggested a suitable expression for the brightness  $h$  of a color: a linear function of the coefficients  $a_{ik}$  and the coordinates of a color.

The main task of color metric then consisted of deriving the coefficients  $a_{ik}$  of the line element, Eq. (34). Schrödinger succeeded in proposing a suitable line element, namely,

$$ds^2 = \frac{1}{\alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3} \left( \frac{\alpha_1 dx_1^2}{x_1} + \frac{\alpha_2 dx_2^2}{x_2} + \frac{\alpha_3 dx_3^2}{x_3} \right) \quad (35)$$

where  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$  denote constants that had to be determined experimentally. With the line element, Eq. (35), the brightness of a color given by the triple  $(x_1 x_2 x_3)$  could be written as

$$h = \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 \quad (36)$$

It obviously satisfied the additivity rule; and it also fulfilled the Weber–Fechner law, since for any two colors, given by the triples  $(x_1 x_2 x_3)$  and  $(x'_1 x'_2 x'_3)$ , respectively, the equation

$$s = \int_{x'_1 x'_2 x'_3}^{x_1 x_2 x_3} ds = \ln \frac{h}{h'} \quad (37)$$

relates the associated brightnesses  $h$  and  $h'$ .

With his specific color metric, Eq. (35), Schrödinger not only provided a reasonable fit to the available data, the fundamental gauge colors having been determined by Arthur Koenig by investigating color-blind people, finding the three constants to assume the values  $\alpha_1 = 43.33$ ,  $\alpha_2 = 32.76$ , and  $\alpha_3 = 1$ ; he also showed how the theory worked in practical situations, such as heterochromous photography.

The work on color metric, which Schrödinger completed in Vienna, certainly interested his colleagues in Jena, a place of great tradition in optical industry, but less so in Stuttgart. However, Schrödinger then moved

to Breslau; and again he found himself in an institute where research on optical phenomena had played an important role, at least from the time Otto Lummer and Ernst Pringsheim had arrived there earlier in the century.

Schrödinger occasionally referred to the fact that at times he turned his attention, during the first half of the 1920s, from problems of quantum physics to those of color theory, out of sheer despair arising from the difficulties of the theory of atomic structure.<sup>(149)</sup> During these years Schrödinger gave his highest devotion to quantum-theoretical problems of atomic structure and, if he failed to make progress in these, he simply relaxed by looking at the less strenuous problems of color theory. Thus, for example, he completed an article in the summer of 1925 on "Visual Sensations" ("*Gesichtsempfindungen*") for the second volume of the new (eleventh) edition of *Müller-Pouillet's Lehrbuch der Physik*.<sup>(150)</sup> In this article of over a hundred pages, organized in 44 sections, Schrödinger discussed—among other things—the conceptions of human light perception in daytime and at dawn, the temporal and spatial psychological effects of light action, and finally threshold perceptions and specific problems of comparing different schemes of color vision and color theory; this work was published only a year later.

In preparing this article and studying the relevant literature, Schrödinger came across several questions which required further investigation. This led him to submit, between the fall of 1924 and the spring of 1925, three papers presenting clarifications of older controversies and several new aspects. The first paper of this series appeared in the *Naturwissenschaften* issue of November 7, 1924 and was entitled "On the Origin of the Sensitivity Curves of the Eye."<sup>(151)</sup> In this article Schrödinger attempted to explain the detailed structure of the normal sensitivity of the human eye for colors, on the one hand, and for low brightness, on the other. A further paper on a related subject, entitled "On the Subjective Colors of Stars and the Quality of Sensation at Dawn,"<sup>(152)</sup> constituted Schrödinger's reply to a question that had been asked by the Babelsberg astronomer Kurt Felix Bottlinger. Bottlinger had emphasized the discrepancy between the color vision of stars and of terrestrial light sources having the same temperature, and had closed with the remark: "It would be interesting to hear once an opinion from the physiological side on this undoubtedly remarkable phenomenon which, to my knowledge, has so far never been discussed."<sup>(153)</sup> Schrödinger's answer appeared in the May 1 issue of *Naturwissenschaften*,<sup>(152)</sup> where Bottlinger had also published his note. Schrödinger claimed that the noted discrepancy might be explained by a complex cooperation of effects from both mechanisms, the cone and the rod mechanisms, at comparatively low light intensities. He especially



argued that the white color point did not coincide in the two mechanisms, thus the white point of the rod mechanisms was seen as some blue point by the cone apparatus—a fact which Schrödinger confirmed by simple experiments carried out at Peter Debye's institute. Consequently, white stars having the surface temperature of the sun appeared during the night as yellow, while stars much hotter than the sun appeared to be white. Still another reason caused the color shift of yellow stars to red ones; any yellow color point possesses in color theory an admixture of fundamental red, and it is this component which remains perceptible. Schrödinger incorporated all these results in his review article for *Müller-Pouillet's Lehrbuch*.<sup>(150)</sup>

At about the same time, Schrödinger became involved in a renewed discussion on the problem of colorimetry, especially after Tadeusz Oryng had partly contradicted, in the February 1 issue of *Physikalische Zeitschrift*,<sup>(154)</sup> the criticism raised by Fritz Kohlrausch against Ostwald's color theory.<sup>(137)</sup> Schrödinger placed himself on the side of his friend Kohlrausch in a note "On Color Measurement."<sup>(155)</sup> In reply to Oryng's claim, that all classical color determination depended heavily on the color perception of the individual observer, Schrödinger remarked: "Is it really impossible to come to an understanding with those who adhere totally or partially to Ostwald's absolute color determination, at least insofar as one cannot determine the *appearance* of a light more absolutely than it *really is*, i.e., only in the approximation in which the color vision of normal persons coincides?"<sup>(156)</sup> All the differences between individual observers did not render the classical methods in color theory useless, but represented "the really existing variation range, even of the normal visual organs, which cannot be abolished and which removes the possibility of an absolute determination—as strictly as for a purely physical quantity—in the case of color."<sup>(156)</sup> What Ostwald and his partisans demanded could therefore never be realized. Hence Schrödinger did not bother to describe Ostwald's theory in his review article but rather declared in his introduction that he was omitting it "due to certain doubts which have been raised against it."<sup>(159)</sup>

Later in 1925 Schrödinger again submitted a further, longer paper on color theory; it was submitted to the Vienna Academy of Sciences at the session of December 17, 1925 and had the title "On the Relation of the Four-Color Theory to the Three-Color Theory."<sup>(158)</sup> The so-called four-color theory rested on the basis of three pairs of contrasting sensations: red-green, yellow-blue, and white-black. Since the four-color theory and its derivatives—like Ostwald's color theory—"was well liked in artistic circles,"<sup>(159)</sup> Schrödinger, in his new paper, did not wish to argue for or against it. He noted: "We are dealing with the mere statement that on a

purely formal level the relation between the two theories—the three-color theory and the four-color theory—can be thought of as an extremely simple one, namely as a mere *transformation of variables*.<sup>(160)</sup> In order to find the desired simple relation explicitly, Schrödinger started from the standard color triangle in the three-color theory, an equilateral triangle with the fundamental colors red, green, and blue as corners and the white point in the center; the spectral colors lay on a curve in the interior of this color triangle with only the wavelengths from 545 to 670  $\mu\text{m}$  falling on the side connecting the red and green corners. Of course, Schrödinger noted, one can also describe the spectral colors and all the other colors (e.g., the pigment colors) by taking a different triangle, which is created from the standard one by a linear coordinate transformation. He then constructed what corresponded to the color triangle in the four-color theory in the following way: two sides were formed by the lines joining the blue and the white points and the red and the white points, respectively; the third side then coincided with a part of the line connecting the colors of zero brightness. The new triangle thus possessed the white point as a corner; the second corner lay on the line connecting red and white away from any real color and was called “original green” (“*Urgrün*”), and the third corner nearly coincided with the fundamental blue point and was called “original blue” (“*Urblau*”) in the four-color theory. In order to represent the content of the four-color theory, one has to convert the new triangle to a quadrangle, which is easily obtained in a straightforward procedure: first, one transforms the triangle white–original green–original blue into a rectangle with the two equal small sides white–original green and white–original blue; these sides then constitute a rectangular coordinate system in the plane, with the white point as origin and the original blue and original green making the unit distances. Opposite the original blue and original green are the corresponding counter colors “original yellow” and “original red” at negative unit distances, respectively. The two pairs original blue–original yellow and original green–original red, together with the third pair black–white, then allow one to describe the colors quantitatively in the four-color theory also and to establish a relation between the three- and four-color theories.

Finally, Schrödinger gave the above results a phylogenetic interpretation and sketched the following picture of color vision. Early in biological evolution animals developed an organ to receive light of a certain (comparatively large) frequency interval; in a second step a refinement of that organ occurred, which enabled the animals to differentiate between lights of shorter and longer wavelengths, respectively. But, “since for the development of an individual differentiation ability for single frequencies the prerequisites were lacking, the most probable was the formation of a

gross differentiation ability; i.e., there was established a particular sensation element making it possible to denote the dominance of the short-wavelength or long-wavelength components, as compared to the "normal" constitution of light (sunlight)."<sup>(161)</sup> This sensation element, Schrödinger claimed, led to a psychological registration of the blue-yellow sequence containing the neutral white point; hence dichromatic vision, which is typical of many animals and also of a part of color-blind human beings, was established. The full trichromatic vision occurred in a third phylogenetic step, in which a further differentiation was introduced dissolving the basic sensation of yellow into a sequence from red to green. All these evolutionary steps, Schrödinger emphasized, can still be traced in the human eye; most peripheral zones of the retina exhibit a gross sensitivity to light with no color differentiation; the inner ones register the blue-yellow difference, and only the innermost regions near the *fovea* display the full sensitivity to human color sensations.

With such general considerations, Schrödinger concluded his last contribution to color theory which he considered, in retrospect, as his most valuable contribution when judging his entire work in this field. "The only important one, it appears to me, is the latest obtained re-recognition of the real meaning of the three- and four-color schemes and their connection with the phylogenesis of color vision," he wrote in his autobiographical sketch for the Nobel Foundation.<sup>(1)</sup> In the development of Schrödinger, the path-breaking scientist, his concern with the problems of color theory and color vision had been extremely important.

## 8. PROBLEMS AND EXTENSIONS OF STATISTICAL MECHANICS

Schrödinger once wrote in an autobiographical note: "In scientific work I have... never followed a strong line, that is, a program guiding me for a long period of time."<sup>(1)</sup> This statement might well be consistent with the variety of problems Schrödinger discussed in his papers during the first half of the 1920s. However, in spite of Schrödinger's disclaimer, one finds a series of ten articles and notes, plus an extended handbook article, contributed between 1921 and early 1926, which really indicate a stronger line in Schrödinger's research; they are all concerned with problems of statistical mechanics. Furthermore, statistical mechanics and the kinetic theory of matter constituted the most favored topics which Schrödinger announced for his lectures at Jena and Breslau, and later on at Zurich; his concern with these problems did indeed constitute a coherent guiding program. Schrödinger's work on statistical mechanics ultimately provided

him with the starting point for getting into and developing wave mechanics.<sup>(162)</sup>

Schrödinger had brought the problem for his first publication in this field from Vienna. It had emerged from a debate on the nature and separability of different isotopes of the same chemical element, which Schrödinger's colleagues George de Hevesy and Friedrich Paneth of the *Institut für Radiumforschung* had carried out with Kasimir Fajans, then at the *Technische Hochschule* in Karlsruhe. Hevesy and Paneth had concluded, on the basis of electrolytical investigations, that different isotopes—say RaE and bismuth—were classically completely equivalent, i.e., “isotopic elements may really replace each other completely, as far as their chemical mass action is concerned.”<sup>(163)</sup> Fajans had, however, argued “that the isotopes must be considered, as far as their chemical mass action is concerned, as independent parts.”<sup>(164)</sup> In the course of his thermodynamical treatment of the problem, Fajans had drawn attention to an important fact: namely, that one must abandon, in the theoretical discussion of the thermodynamical behavior of isotopes, “the usual auxiliary tools, like semipermeable walls or solvents which dissolve substances to a different degree.”<sup>(165)</sup> Still, this criticism did not convince Viennese scientists, and the debate dragged on for over a year without producing a satisfactory clarification of the problem. On two occasions, i.e., on March 18 and November 22, 1920, George de Hevesy presented his new results on the properties of isotopes at the meetings of the *Gauverein* of the German Physical Society.

Schrödinger attended the first of these meetings while he was still in Vienna. About a year later he submitted a paper, “Isotopy and Gibbs' Paradox,” to *Zeitschrift für Physik*.<sup>(166)</sup> Schrödinger started explicitly from the previous discussion between de Hevesy and Paneth on the one hand, and Fajans on the other, summarizing the result as “thermodynamical diversity of isotopes in principle, in spite of their complete or nearly complete chemical replaceability.”<sup>(167)</sup> However, he contradicted a result which Fajans had obtained, stating that the energy set free by the mixing or diffusion of the volumes, containing different isotopes of the same chemical element, was proportional to the difference of their respective atomic weights—hence, it should become arbitrarily small as the mass difference disappeared. Schrödinger claimed that one could conduct “a thought experiment in which there takes place a reversible, isothermal process of mixing of two (chemically noninteracting) gases; hence the full amount of [mixing] energy could be gained as long as a finite difference of the molecular weights exists at all; and this amount is not related at all to the magnitude of this difference.”<sup>(167)</sup> This independence of the mixing energy from the weight difference of the isotopes evidently gave rise to the

situation which Josiah Willard Gibbs had discussed at the very end of his book on statistical mechanics.<sup>(168)</sup>

In order to prove his assertion, Schrödinger started with two identical volumes of magnitude  $V_0$ , each of which was filled with one gram-atom of different isotopes, having molecular weights  $M$  and  $M'$ , at the same temperature. He then brought the volume containing isotopes of mass  $M'$  ( $< M$ ) isothermally to a higher position (the volume  $V_0$  was thereby increased to  $V_1$ ) and established a connection with the vessel containing molecules of mass  $M$  using a very thin tube (whose volume can be neglected); as a consequence a distribution of the isotopes in agreement with the barometric formula was reached. Finally, he reduced, again isothermally, the upper volume to zero, thus producing a homogeneous mixture of all molecules  $M$  and  $M'$  in the lower volume  $V_0$ . The energy consumed in the entire process could be calculated and found to be zero. In order to arrive at the situation of the usual mixture of isotopes, Schrödinger then simply let the volume  $V_0$  expand to  $2V_0$ . He concluded: "We . . . thus can win *from the reversible mixture at constant volume altogether the energy amount  $RT \ln 2$* , at the expense of the heat of the surroundings, just as is well known from treating any two chemically different gases (which do not react with each other) by the method of semipermeable walls."<sup>(169)</sup>

More than a year later, in September 1922, Schrödinger sent a further paper, dealing with a problem of the kinetic theory, to *Zeitschrift für Physik*.<sup>(170)</sup> He derived the stimulus for the new work from two papers on the theory of solids that had been published in the same journal more than a year previously. Max Born and E. Brody of Göttingen had tried at that time to explain the deviations of the specific heats of monatomic solids from the classical value (according to the rule of Dulong and Petit) at extremely high temperatures by taking into account finite amplitudes of the lattice vibrations.<sup>(171)</sup> It was not Schrödinger's intention to replace (by his contribution) the methods developed by Born and Brody in Göttingen; he only wished to obtain their results by simpler means. That is, unlike Born and Brody, he did not expect to establish a new, fundamental scheme, but simply hoped to contribute a modest share to the specific questions of statistical and kinetic theory. The paper of September 1922 showed explicitly Schrödinger's continuing interest in the problem of the specific heats of solids. It further showed that he followed rather carefully the literature in this field, which provided him once in a while with the opportunity to contribute a small piece of work by improving an earlier result. As he later characterized his procedure: "Rarely is my word the first [answer to a question], but it is often the second, and it is stimulated by the desire to contradict or to correct, even if later the systematic continuation [of my answer] turns out to be far more

essential than the contradiction which only served to start the whole theory.”<sup>(1)</sup> This characterization also applied to another note on a statistical problem,<sup>(172)</sup> which again arose from a study of the literature; in this note, Schrödinger improved upon a work of Léon Brillouin<sup>(173)</sup> dealing with the thermal equilibrium between light and acoustic rays.

The three papers on questions of statistical mechanics mentioned above arose from rather different stimulations. Still, they formed part of Schrödinger's strong involvement at that time in the general statistical description of matter. In fact, they indicated, together with a few other publications on the subject, only the visible tip of the iceberg of Schrödinger's very deep-rooted interests in that field. Thus, for instance, from his unpublished notes we learn that he planned to write a comprehensive text on the kinetic theory of matter; there exists a draft of the detailed organization for a book on “Molecular Statistics” (“*Molekularstatistik*”). In addition, there exist among Schrödinger's papers extensive manuscripts dealing with the chemical constant and gas degeneracy, with the quantum statistical method of Darwin and Fowler, and with detailed lecture notes on quantum statistics.<sup>(174)</sup> One wonders why these efforts did not result in Schrödinger's writing one of the handbook articles on the kinetic theory of matter, classical statistics, or quantum statistics. Indeed his plans and outlines agreed rather well, if not coincided, with some of the reviews given by his contemporaries in the physics handbooks and encyclopedias which were published in the 1920s. For example, what Schrödinger sketched in his notes on quantum statistics showed a considerable similarity with what Adolf Smekal presented, under the title “General Foundations of Quantum Statistics and Quantum Theory,” for the *Encyklopädie der mathematischen Wissenschaften*.<sup>(175)</sup> On the other hand, many topics in Schrödinger's detailed outline of the chapters and sections of a proposed book on “*Molekularstatistik*” were discussed in a review article, which his other Viennese fellow-countryman Karl Herzfeld had composed for the third volume of *Müller-Pouillet's Lehrbuch der Physik*.<sup>(176)</sup> It seems that all available requests for handbook articles had already been sent out to other authors, and Schrödinger was forgotten. Still, he possibly considered writing a separate book on kinetic theory and quantum statistics, but evidently did not find the time to do so. Thus the only larger publication, which resulted from his efforts with these topics, was a review article entitled “Specific Heats. Theoretical Part.”<sup>(177)</sup> Schrödinger had already published two articles on the problem of specific heats in his Vienna days.<sup>(87,88)</sup> Especially the second article in *Physikalische Zeitschrift* constituted a veritable review devoted to the specific heats of solids,<sup>(88)</sup> and the new article which was contributed to the *Handbuch der Physik*<sup>(177)</sup> could partly be considered as a modernized extension of this review.

In 1924 Schrödinger submitted two papers to *Zeitschrift für Physik* dealing with the question of specific heats. In the first one, a two-page note on "Remarks on Two Papers of Mr. Elemér Császár on Radiation Theory and Specific Heats," Schrödinger found that Császár's results on the specific heats of solids—based on the latter's quantum hypothesis—did not agree with Debye's formula, i.e., with experience.<sup>(178)</sup> The second paper on specific heats, also published in 1924, dealt with the hydrogen molecule.<sup>(179)</sup> The paper on the specific heat of molecular hydrogen exhibited many of the features characteristic of the work of Schrödinger: he again took a well-known theoretical model of the hydrogen molecule—namely, one in which the system of two nuclei performs an ordinary rotation about the axis with half-integral quantum number  $(2n - 1)$ ,  $n$  being an integer—and thoroughly discussed the consequences from a definite (new) assumption; he then compared the theoretical results in the most suitable way—i.e., in a way in which the assumed hypothesis could be submitted to the sharpest test—with the available data; thus, he derived conclusions about the validity of a theory which were as reliable as possible in the situation considered.<sup>(180)</sup> Schrödinger gave a discussion of the relevant experimental and theoretical results available in the literature, and referred to his paper on the specific heat of the hydrogen molecule<sup>(179)</sup> in his review article on specific heats in *Handbuch der Physik*.<sup>(177)</sup>

In December 1923, about a year before the above-mentioned paper on the specific heat of the hydrogen molecule, Schrödinger submitted a paper to the *Physikalische Zeitschrift* on "Gas Degeneracy and the Mean Free Path," which was published in the issue of January 15, 1924.<sup>(181)</sup> The problem treated by Schrödinger again belonged among the topics that he had mentioned explicitly in the outline of his planned book on "*Molekularstatistik*." In his notes, Schrödinger had given some details of a chapter on "chemical constant and gas degeneracy." The connection between the two problems, i.e., the chemical constant and gas degeneracy, might appear on first inspection a little surprising. Yet, historically, both topics originated from the same source, namely the so-called third law of thermodynamics or the heat theorem. Walther Nernst, the inventor of the theorem, had discussed many of its consequences in a lecture "On More Recent Problems of Heat Theory," presented on January 26, 1911 to the Prussian Academy of Sciences.<sup>(182)</sup> He pointed out for the first time the necessity of quantizing, besides the vibrations, the rotations of di- and polyatomic gas molecules also. Finally, Nernst pointed out that the deviations from the laws of classical mechanics in the case of the translational motion of gas molecules could be described by applying the quantum hypothesis. Nernst's talk at Berlin immediately stimulated not only the development of a quantum theory of rotations, but also attempts at a

quantization of the translational motion of atoms, molecules, and electrons. The main results of these attempts were the theory of the so-called chemical constant, developed between 1911 and 1919 by Otto Sackur, Hugo Tetrode, and Otto Stern, and several theories of ideal gases at low temperatures which exhibited deviations from the classical formula. Fritz Reiche, Schrödinger's successor in the chair of theoretical physics at Breslau, had given a fine summary of these results in his book *Die Quantentheorie: Ihr Ursprung und Ihre Entwicklung*.<sup>(183)</sup> Reiche had emphasized that "the attempts to apply [quantum theory] to the translational energy of gases rest upon a much more insecure basis [than the attempts at a quantization of the rotational energy]"; and also that this step was necessary to remove "the hitherto exceptional position occupied by monatomic gases, whose molecules contain only translational energy..., for they, too, must succumb to the quantum law."<sup>(184)</sup> He had then displayed the main aspects and results of the quantum theories of ideal monatomic gases proposed by Otto Sackur, Hugo Tetrode, Willem Hendrik Keesom, Wilhelm Lenz and Arnold Sommerfeld, Paul Scherrer, Max Planck, and Walther Nernst.

In December 1923 Schrödinger joined in at essentially this stage of the development. Citing Reiche's book as the source of reference to the earlier literature, he first stressed the central role played by a characteristic temperature  $\Theta$ —similar to the one occurring in Debye's theory of the specific heat of solids—in all previous discussions of gas degeneracy. This temperature was given by the relation

$$\Theta = \frac{h^2}{8ml^2k} \quad (38)$$

where  $h$  and  $k$  denoted Planck's and Boltzmann's constant, respectively,  $m$  is the mass of a gas molecule, and  $l$  a characteristic length. The above-mentioned theories now split into two different classes, in which  $l$  and  $\Theta$  assumed very different orders of magnitude. Thus the theories of Tetrode, Keesom, Sommerfeld and Lenz, and Nernst yielded  $l \sim (V/N)^{1/3}$ , i.e., a characteristic length having the same order of magnitude as the average distance between the molecules; on the other hand, the theory of Paul Scherrer in Göttingen—now Schrödinger's colleague in Zurich—rather suggested  $l \sim V^{1/3}$ , i.e., a macroscopic characteristic length.<sup>(185)</sup> Schrödinger did not find both results acceptable. The first, in particular, led to comparatively high characteristic temperatures, i.e.,  $\Theta \sim IK/M$  (where  $M$  denoted the molecular weight of the gas under consideration), which should give rise to degeneracy effects inconsistent with the available data. The second class of theories did not cause such difficulties, as it implied a



much smaller  $\Theta$ ; but they resulted in the unsatisfactory conclusion that "twice the amount of gas in exactly the same state would not exhibit exactly the same properties"<sup>(186)</sup>; hence quantum effects would show up only for a highly dilute gas in very small volumes, i.e., as a kind of surface effect. Schrödinger now proposed a different order of magnitude for  $l$ , lying between the previously suggested possibilities. He argued: "For me, therefore, there has never existed any doubt about the fact that, e.g., in the gas model of Scherrer one should logically take for  $l$  a quantity of the order of magnitude of the mean free path [of the molecules]."<sup>(186)</sup>

Schrödinger then presented the "rough sketch of a theory... which demonstrates that the identification of the characteristic length with the mean free path is not at variance with experience."<sup>(186)</sup> He hoped that the use of the mean free path in Eq. (38) would reduce the characteristic temperature to the order of  $10^{-14}$  K for gas molecules, thus being consistent with the known observations. Schrödinger considered a system (model) of  $N$  gas atoms (mass  $m$ ) in a volume  $V$  at temperature  $T$  and imposed on their velocity the quantum condition

$$2mv_n\lambda = nh \quad (n = 1, 2, \dots) \quad (39)$$

where  $\lambda$  denotes the mean free path of atoms. He obtained the partition function,

$$\begin{aligned} \psi &= Nk \ln \left[ \frac{\pi}{2} \frac{V}{\lambda^3} \sum_{n=1}^{\infty} n^2 \exp \left( -n^2 \frac{\Theta}{T} \right) \right] \\ &\approx \frac{3}{2} Nk \ln(V^{2/3}T) + Nk \ln \frac{(2\pi mk)^{3/2}}{h^3} \end{aligned} \quad (40)$$

involving the characteristic temperature

$$\Theta = \frac{h^2}{8m\lambda^2k} \quad (41)$$

Further, the mean free path had disappeared in the final expression for  $\psi$ , and also for the entropy  $S$ , i.e.,

$$S = \frac{3}{2} Nk \ln(V^{2/3}T) + NK \ln \frac{(2\pi mek)^{3/2}}{h^3} \quad (42)$$

where  $e$  denotes the base of the natural logarithm. The chemical constant would, therefore, not depend on  $\lambda$ .

The relation for the characteristic temperature, Eq. (41), was indeed the one which Schrödinger had hoped to find; by inserting  $\lambda \approx 10^{-5}$  cm it

yielded  $\Theta = 10^{-4}$  K. Schrödinger also confirmed a suggestion that Keesom had made, namely, that a degenerate electron gas would not contribute to the specific heats of metals<sup>(187)</sup>; by taking a mean free path of  $10^{-7}$  to  $5 \times 10^{-8}$  cm for electrons in metals,  $\Theta$  assumed values between 4,500 and 18,000 K.

Schrödinger devoted the most detailed discussion to another result of his calculation. The formula for the entropy, Eq. (42), deviated from the one which Max Planck had been propagating for years by an additional term,  $Nk \ln(N!)$ . Hence the statistical probability of Schrödinger's gas model differed from Planck's thermodynamic probability by a factor of  $1/N!$ . Schrödinger was not disturbed by this difference, as he had doubted the correctness of this factor for some time. As early as December 1900, Max Planck had introduced the factor  $N!$  into his derivation of the blackbody radiation law on the basis of a statistical distribution of  $N$  equal energy packets of radiation among the resonators in a cavity.<sup>(188)</sup> Planck had used the same division by  $N!$  for like particles in his quantum theory of monatomic gases.<sup>(189)</sup> Then, however, Paul Ehrenfest and Victor Trkal, in a paper published in 1920, called the introduction of the factor  $(N!)^{-1}$  "obscure."<sup>(190)</sup> By following the statistical rules of Boltzmann, Ehrenfest and Trkal had arrived at expressions for the probability which did not contain the dividing factor.

Schrödinger treated the problem of the factor  $(N!)^{-1}$ , and the related problem of the definition of the absolute entropy, in an unpublished manuscript on "*Chemische Konstante und Gasentartung. II.*" He sketched there in detail Planck's procedure of defining the thermodynamic probability and noted several shortcomings. Being convinced about the mistakes in Planck's treatment of statistical methods, Schrödinger tended to the opinion that Ehrenfest and Trkal's doubts against Planck's factor  $(N!)^{-1}$  were justified. He was therefore not at all surprised when he found, in his paper of December 1923,<sup>(181)</sup> that, in his thermodynamic probability for the ideal quantum gas, this factor was not included, and he defended this result. Thus the entropy of  $N$  condensed (degenerate) atoms in his model was not zero—as in Planck's—but rather  $k \ln(N!)$ . In spite of favoring the point of view taken by Ehrenfest and Trkal, Schrödinger thought about an "Attempt to Correct Planck's Error" in his unpublished notes. But he did not get very far in 1923 in rescuing Planck's method. About two years later, however, in a paper entitled "Remarks on the Statistical Entropy Definition of an Ideal Gas," which he sent to the Prussian Academy of Sciences and which was presented by Max Planck to the meeting of July 23, 1925, he proposed several possibilities for the definitions of the entropy, including Planck's.<sup>(191)</sup>

What had caused Schrödinger to undertake these renewed efforts? In

August 1924 the *Zeitschrift für Physik* had published an article "*Planck's Gesetz und Lichtquantenhypothese*" ("Planck's Law and the Light-Quantum Hypothesis") by Satyendra Nath Bose, in which Bose suggested a new derivation of Planck's radiation law based on a new statistical method for light-quanta.<sup>(192)</sup> Albert Einstein had not only translated the paper by the Indian physicist, but also immediately applied his method in developing a new theory of ideal gases, in a communication presented to the Prussian Academy of Sciences on July 10, 1924, entitled "Quantum Theory of the Monatomic Ideal Gas."<sup>(193)</sup> He had shown in this theory, which he extended in two further contributions to the Prussian Academy of Sciences,<sup>(194,195)</sup> that a monatomic gas indeed exhibited, at very low temperatures, deviations from the (classical) ideal gas law or degeneracy, and that the entropy of the gas was described essentially by Planck's method. Since these new results in quantum statistical theory were obviously important and had to be taken seriously, Schrödinger renewed his previous attempts to correct "Planck's errors" and arrive at a more consistent derivation of Planck's entropy expression. He summarized the results of this endeavor in his new paper in the summer of 1925, in which he considered four entropy definitions.<sup>(191)</sup>

Schrödinger first discussed three entropy definitions for a quantum-theoretical gas of  $N$  atoms, which possess discrete energy states given by 1, 2, 3,...—with  $N_i$  atoms being in the  $i$ th state—in a given volume having a given total entropy. The first entropy definition was given by the relation

$$S_I = k \ln W_{\max} \quad (43)$$

where  $W_{\max}$  was the maximum of the permutation number expression

$$W = \frac{N!}{N_1! N_2! \cdots N_i! \cdots} \quad (44)$$

He criticized this definition, for it could apply only at very low temperatures because: "As soon as the number of occupiable energy states is *larger* than the number of molecules—and this number is quite extraordinarily larger, except for extremely low temperatures— $W_{\max}$  will become equal to  $N!$ ; hence,  $S_I$  would be independent of the energy content  $E$ , which is meaningless."<sup>(196)</sup> Hence he proposed a second entropy definition, namely,

$$S_{II} = k \ln \sum W \quad (45)$$

in which the sum is taken over all permutation numbers, Eq. (44). The definition, Eq. (45), coincided with  $S_I$ , Eq. (43), for very large molecule

numbers. Finally, he introduced a third definition of the entropy,  $S_{\text{III}}$ , by taking a large number  $n$  of gas systems, each consisting of  $N$  atoms, etc., by

$$S_{\text{III}} = \frac{S_1^{(1)} + S_1^{(2)} + \cdots + S_1^{(n)}}{n} \quad (46)$$

with  $S_1^{(i)}$  the entropy of the  $i$ th system according to the first definition. Thus Schrödinger established on safe grounds the fact that the average entropy per system,  $S_{\text{III}}$ , coincided with  $S_{\text{II}}$ . Schrödinger claimed that, since  $S_{\text{II}}$  could be considered as the correct continuation of  $S_1$  into the region of higher temperatures (it agreed with  $S_1$  for lower ones), the second entropy definition, Eq. (45), should be taken as the basis of all further considerations. Still, it differed from Planck's; to arrive at the latter one had to take

$$S = S_{\text{II}} - k \ln(N!) \quad (47)$$

Schrödinger noted: "I do *not* intend *here*—as I have done elsewhere<sup>(181)</sup>—to fight this interpretation [of Planck], but *will consider it to be the correct one*. I wish to attempt a demonstration that, *if* one assumes it, one is *automatically* led to that definition of the entropy of the ideal gas, which has recently been introduced by A. Einstein<sup>(193–195)</sup> and soon thereafter, apparently independently, by A. Schidlof,<sup>(197)</sup> on the basis of a type of statistics, which at first inspection seems to be very strange."<sup>(198)</sup>

Schrödinger was more ambitious than just taking Planck's subtraction procedure for granted, especially since he did not agree with its justification. He rather claimed: if one wants to count two states, which are related to each other by molecules exchanging their roles, as one state, then it would not suffice to divide the permutation number by  $N!$ . "*In order that two molecules are able to exchange their roles,*" he wrote, "*they must really have different roles; otherwise we have just not counted such states as being different in their earlier enumeration; hence, we need not and also should not 'correct away' a multiplicity, which had not previously existed for us at all!*"<sup>(198)</sup>

In following this concept, one had to adopt a new procedure: one had to divide in the earlier expression, Eq. (45), each permutation number  $W$  by itself; hence each term in the sum should be replaced by unity, and the new, fourth entropy definition

$$S_{\text{IV}} = k \ln(\text{number of all distributions for a given total energy}) \quad (48)$$

resulted. This entropy definition, Schrödinger claimed, would now be identical with the one proposed by Einstein and Schidlof; besides, it agreed at

low temperatures with Planck's definition, Eq. (47). Schrödinger remarked: "*The transition from [(45)] to [(48)] is therefore really nothing more than the logical continuation of Planck's division—which, for high temperatures, is assumed to be statistically founded—to the region of temperatures which are so low that the occasional multiple occupation of single quantum states cannot be neglected any longer.*"<sup>(198)</sup> Planck's entropy for the ideal gas, he argued, did not really go to zero at absolute zero temperature but to a negative value,  $-k \ln(N!)$ , an impossible result since the permutation number  $W$  had to be "at any rate a *natural number* [an integer]"; thus "one is led nearly cogently to Einstein's form of statistics if one wants to give a statistical foundation for Planck's 'division by  $N!$ .'"<sup>(199)</sup>

In closing the paper, Schrödinger hinted at a "totally different path" ("*ganz anderen Weg*"),<sup>(199)</sup> on which one might also obtain the desired result, namely the method of dealing not with the energy states of individual gas atoms but from the very beginning with only the energy states of the whole system of  $N$  atoms. This method had already been applied earlier, especially by Max Planck in the 1916 paper on the quantum theory of monatomic gas.<sup>(189)</sup> When studying that method in the summer of 1925, Schrödinger discovered several difficulties, which he considered "so large as to render impossible an execution of the beautiful idea: that is, do not begin with the quantization of single molecules but with that of the whole gas."<sup>(200)</sup> However, in December 1925 he had overcome these large difficulties; he would then present a solution to the problem of deriving Einstein's statistics on the basis of the "beautiful idea" in two papers,<sup>(201,202)</sup> which were intimately connected with the origin of wave mechanics.

## PRINCIPAL BIBLIOGRAPHY

Jagdish Mehra and Helmut Rechenberg: *The Historical Development of Quantum Theory*, Volume 5: *Erwin Schrödinger and the Rise of Wave Mechanics, 1887–1926*, Parts 1 and 2, Springer-Verlag, New York (1987).

## REFERENCES

1. Erwin Schrödinger, in *Les Prix Nobel en 1933*, Imprimerie Royale P. A. Norstedt & Soener, Stockholm: (1935), pp. 86–88; reprinted in *Gesammelte Abhandlungen/Collected Papers* 4 (1984), pp. 361–363.
2. AHQP Interview with Mrs. Annemarie Schrödinger, April 5, 1963, pp. 1–2.
3. E. Schrödinger, "*Lebenslauf*," an autobiographical note by Schrödinger, dated July 2, 1938, AHQP Microfilm No. 39, Section 1.
4. E. Schrödinger, *Gedichte*, Kupper, Bad Godesberg (1949).

5. E. Schrödinger, *Nature and the Greeks*, University Press, Cambridge (1954) (elaborated Shearman Lectures, delivered at University College, London, on May 24, 26, 28, and 31, 1948).
6. For a list of these courses, see J. Mehra and H. Rechenberg: *The Historical Development of Quantum Theory*, Volume 5, Part 1. Springer-Verlag, New York (1987), pp. 69–70.
7. Paul Ehrenfest moved with his Russian-born wife Tatyana to Göttingen and later to St. Petersburg. Lise Meitner served, after receiving her doctorate, first as a teacher in a girls' secondary school in Vienna, then went on to Berlin to pursue a scientific career there.
8. E. Schrödinger, Antrittsrede, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. C–CII (presented at the meeting of July 4, 1929); reprinted in *Collected Papers* 4 (1984), pp. 303–305.
9. See the announcement in *Phys. Z.* 9, 696 (1908), and 10, 294 (1909). Schrödinger kept two notebooks on Prizbram's lectures (AHQP Microfilm No. 39, Section 1).
10. F. Hasenöhl, "Über die Anwendbarkeit der Hamiltonischen partiellen Differentialgleichung in der Dynamik Kontinuierlich verbreiteter Massen," *Festschrift Ludwig Boltzmann*, J. A. Barth, Leipzig (1904), pp. 642–646.
11. E. Schrödinger, Über die Leitung der Elektrizität auf der Oberfläche von Isolatoren an feuchter Luft, *Sitz. Ber. Akad. Wiss. (Wien)* 119, 1215–1222 (1910); reprinted in *Collected Papers* 2 (1984), pp. 3–9.
12. E. Schrödinger, Zur kinetischen Theorie des Magnetismus (Einfluß der Leitungselektronen), *Sitz. Ber. Akad. Wiss. (Wien)* 121, 1305–1328 (1912); reprinted in *Collected Papers* 1 (1934), pp. 3–26.
13. Nearly fifteen years later Wolfgang Pauli, Schrödinger's younger Viennese countryman, would start the consistent explanation of the phenomena with his paper on the paramagnetism of metal electrons, W. Pauli, Über Gasentartung und Paramagnetismus, *Z. Phys.* 41, 81–102 (1926); reprinted in *Collected Scientific Papers* 2 (1964), pp. 284–305.
14. E. Schrödinger, Studien über Kinetik der Dielektrika, den Schmelzpunkt, Pyro- und Piezoelektrizität, *Sitz. Ber. Akad. Wiss. (Wien)* 121, 1937–1972 (1912); reprinted in *Collected Papers* 1 (1984), pp. 63–78.
15. E. Schrödinger, Ref. 14, pp. 1937–1938.
16. Ludwig Boltzmann displayed in detail van der Waals' theory of gaseous and fluid states in the second volume of his *Vorlesungen über Gastheorie*. He did not address there the problem of the solid state at all, nor did he publish anything on it later (or earlier). However, in the Boltzmann *Nachlaß* a manuscript, entitled "Versuche einer Theorie des festen Körpers vom Standpunkte der mechanischen Wärmetheorie" ("Attempts at a Theory of Solids from the Point of View of the Mechanical Theory of Heat") has been found. In this manuscript Boltzmann dealt with the law of Pierre Louis Dulong and Alexis Thérèse Petit for the specific heats of solids; he tried to derive it on the basis of the assumption that the solids consist of molecules performing thermal vibrations about their average positions. (See G. Fasol, Comments on some manuscripts by Ludwig Boltzmann, in *Ludwig Boltzmann Gesamtausgabe*, Volume 8, R. Sexl and J. Blackmore, eds., Akademische Druck- und Verlagsanstalt, Graz, and Friedr. Vieweg & Sohn, Braunschweig-Wiesbaden (1982), pp. 87–95.)
17. P. Debye, Einige Resultate kinetischen Theorie der Isolatoren, *Phys. Z.* 13, 97–100 (1912); Nachtrag zur Notiz über eine kinetische Theorie der Isolatoren, *Phys. Z.* 13, 295 (1912).
18. Experiments—Debye quoted, e.g., an investigation by the young Hasenöhl (Über den Temperaturcoefficienten der Dielektricitätsconstante in Flüssigkeiten und die Mosotti-Clausius'sche Formel, *Sit. Ber. Akad. Wiss. (Wien)* 105, 460–476 (1906), doctoral dissertation, presented at the meeting of November 9, 1896)—had demanded such a temperature-dependent term.

19. P. Debye, Ref. 17, p. 99.
20. E. Schrödinger, Ref. 14, pp. 1938–1939.
21. P. Weiss, L'hypothèse du champ moléculaire et la propriété ferromagnétique, *J. Phys. (Paris) (4)* **6**, 661–690 (1907).
22. E. Schrödinger, Ref. 14, p. 1943.
23. E. Grüneisen, Zur Theorie einatomiger fester Körper, *Phys. Z.* **12**, 1023–1028 (1911) (presented at the 83rd *Naturforscherversammlung* in Karlsruhe, September 24–30, 1911).
24. P. Debye, Les particularités des chaleurs spécifiques à basse température, *Arch. Sci. Phys. Nat. (Genève)* **33**, 256–258 (1912); Zur Theorie der spezifischen Wärmen, *Ann. Phys. (4)* **39**, 789–838 (1912); Interferenz von Röntgenstrahlen und Wärmeübertragung, *Ann. Phys. (4)* **43**, 49–95 (1914); Zustandsgleichung und Quantenhypothese mit einem Anhang über Wärmeleitung, in *Vorträge über die kinetische Theorie der Materie und der Elektrizität* (Planck, Debye, Nernst, Smoluchowski, Sommerfeld, Lorentz, etc., 1914), pp. 17–60.
25. M. Born, Über die Methode der Eigenschwingungen in der Theorie der spezifischen Wärme, *Phys. Z.* **15**, 185–191 (1914). M. Born and T. von Kármán: Über Schwingungen in Raumgittern, *Phys. Z.* **13**, 297–309 (1912); Zur Theorie der spezifischen Wärme, *Phys. Z.* **14**, 15–19 (1913); Über die Verteilung der Eigenschwingungen von Punktgittern, *Phys. Z.* **14**, 65–71 (1913).
26. E. Schrödinger, *Dielektrizität*, in *Handbuch der Elektrizität und des Magnetismus* (L. Graetz, ed.), Volume I, J. A. Barth, Leipzig (1918), pp. 157–231; reprinted in *Collected Papers* **2** (1984), pp. 216–276.
27. E. Schrödinger, Notiz über die Theorie der anomalen elektrischen Dispersion, *Verh. Deutsch. Phys. Ges. (2)* **15**, 1167–1172 (1913); reprinted in *Collected Papers* **1** (1984), pp. 79–123.
28. Egon von Schweidler, Studien über die Anomalien im Verhalten der Dielektrika, *Sitz. Ber. Akad. Wiss. (Wien)* **116**, 1019–1080 (1907).
29. P. Debye, Zur Theorie der anomalen Dispersion im Gebiete der langwelligen elektrischen Strahlung, *Verh. Deutsch. Phys. Ges. (2)* **15**, 777–793 (1913).
30. P. Drude, Zur Theorie der anomalen elektrischen Dispersion, *Ann. Phys. (3)* **64**, 131–158 (1898).
31. Schrödinger was fairly convinced that the description of the anomalous dispersion was more complicated than Debye had assumed; he suggested, for example, considering besides the permanent dipoles one type of aperiodically damped electrons, as Paul Drude had assumed—this would provide more constants to fit into experimental data than Debye's theory; he also thought that “a simple, generally valid, electric dispersion formula was excluded from the very beginning” (E. Schrödinger, Ref. 27, p. 1170).
32. E. von Schweidler, Atmosphärische Elektrizität, *Encycl. d. math. Wiss. VI/1*, 1918, pp. 235–265, p. 236.
33. E. Schrödinger, Über die Höhenverteilung der durchdringenden atmosphärischen Strahlung (Theorie), *Sitz. Ber. Akad. Wiss. (Wien)* **121**, 2391–2406 (1912).
34. E. Schrödinger, Ref. 33, p. 2391.
35. A. S. Eve, On the Ionization of the Atmosphere due to Radioactive Matter, *Philos. Mag. (6)* **21**, 26–40 (1911); L. V. King, Absorption Problems in Radioactivity, *Philos. Mag. (6)* **23**, 242–250 (1912).
36. E. Schrödinger, Ref. 33, p. 2392.
37. E. Schrödinger, Radium-A-Gehalt der Atmosphäre in Seeham 1913, *Sitz. Ber. Akad. Wiss. (Wien)* **122**, 2023–2067, 2023 (1913).
38. V. F. Hess, Absolutbestimmungen des Gehaltes der Atmosphäre an Radiuminduktion, *Sitz. Ber. Akad. Wiss. (Wien)* **119**, 145–195 (1910).
39. E. Schrödinger, Ref. 37, p. 2048.
40. A. Haas, Über die elektrodynamische Bedeutung des Planck'schen Strahlungsgesetzes

- und über eine neue Bestimmung des Elektrischen Elementarquantums und der Dimensionen des Wasserstoffatoms, *Sitz. Ber. Akad. Wiss. (Wien)* **119**, 119–144 (1910).
41. H. A. Lorentz, Alte und neue Fragen der Physik, *Phys. Z.* **11**, 1234–1257 (1910) (Wolfskehl lectures, delivered October 24–29, 1910 at Göttingen, elaborated by M. Born).
  42. A. Schidlof, Zur Aufklärung der universellen elektrodynamischen Bedeutung der Planckschen Strahlungskonstanten  $h$ , *Ann. Phys. (4)* **35**, 90–100 (1911).
  43. F. Hasenöhl, Über die Grundlagen der mechanischen Theorie der Wärme, *Phys. Z.* **12**, 931–935 (1911) (presented on September 25, 1911 at the 83rd *Naturforscherversammlung* in Karlsruhe).
  44. K. Herzfeld, Über ein Atommodell, das die Balmer'sche Wasserstoffserie aussendet, *Sitz. Ber. Akad. Wiss. (Wien)* **121**, 593–601 (1912).
  45. K. Herzfeld, Der Zeeman effekt in den Quantentheorien der Serienspektren, *Phys. Z.* **15**, 193–198 (1914).
  46. N. Bohr, On the Constitution of Atoms and Molecules, *Philos. Mag. (6)* **26**, 1–25 (1913); reprinted in *Collected Works* **2** (1981), pp. 161–185.
  47. H. Thirring, Zur Theorie der Raumgitterschwingungen und der spezifischen Wärme fester Körper, *Phys. Z.* **14**, 867–873 (1913).
  48. E. Madelung, Molekulare Eigenschwingungen, *Nachr. Ges. Wiss. Göttingen*, pp. 100–106 (1909); Molekulare Eigenschwingungen. Nachtrag zu meiner früheren Mitteilung, *Nachr. Ges. Wiss. Göttingen*, pp. 43–58 (1910); Molekulare Eigenschwingungen, *Phys. Z.* **11**, 898–905 (1910).
  49. A. Einstein, Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme, *Ann. Phys. (4)* **22**, 180–190 (1906).
  50. Debye assumed, in particular, that the sum of all frequency modes up to  $\nu_m$  should be equal to the number of degrees of freedom in the crystal, i.e.,  $6N$ .
  51. See M. Born and T. von Kármán, 1912, Ref. 25, p. 308, Eq. (50).
  52. H. Thirring, Ref. 47, p. 868.
  53. H. Thirring, Raumgitterschwingungen und spezifischen Wärme fester Körper. I, *Phys. Z.* **14**, 127–133 (1914); II, *Phys. Z.* **15**, 180–185.
  54. H. Thirring, Erwin Schrödinger zum 60. Geburtstag, *Acta Phys. Austriaca* **1**, 105–109 (1947).
  55. W. Friedrich, P. Knipping, and M. Laue, Interferenz-Erscheinungen bei Röntgenstrahlen, *Sitz. Ber. Akad. Wiss. (München)*, pp. 303–322 (1912).
  56. M. von Laue and F. Tank, Die Gehalt der Interferenzpunkte bei den Röntgenstrahlinterferenzen, *Ann. Phys. (4)* **41**, 1003–1011 (1913).
  57. M. von Laue and F. Tank, Ref. 56, p. 1010.
  58. M. von Laue, Über den Temperatureinfluß bei den Interferenzerscheinungen an Röntgenstrahlen, *Ann. Phys. (4)* **42**, 1561–1571 (1913).
  59. P. Debye, Interferenz von Röntgenstrahlen und Wärmebewegung, *Ann. Phys. (4)* **43**, 59–95 (1914).
  60. E. Schrödinger, Über die Schärfe der mit Röntgenstrahlen erzeugten Interferenzbilder, *Phys. Z.* **15**, 79–86 (1914); reprinted in *Collected Papers* **2** (1984), pp. 17–24.
  61. E. Schrödinger, Ref. 60, p. 79.
  62. E. Schrödinger, Ref. 60, p. 85.
  63. E. Schrödinger, Ref. 60, p. 86.
  64. E. Schrödinger, Zur Theorie des Debyeeffekts, *Phys. Z.* **15**, 497–503 (1914); reprinted in *Collected Papers* **2** (1984), pp. 17–24.
  65. E. Schrödinger, Ref. 64, p. 498.
  66. E. Schrödinger, Ref. 64, p. 500.



67. M. von Laue and J. S. van der Lingen, Experimentelle Untersuchungen über Debye-effekt, *Phys. Z.* **15**, 75–77 (1914).
68. E. Schrödinger, Zur Dynamik elastisch gekoppelter Punktsysteme, *Ann. Phys. (4)* **44**, 916–934 (1914); reprinted in *Collected Papers 1* (1984), pp. 124–142.
69. L. Boltzmann, *Populäre Schriften*, J. A. Barth, Leipzig (1905).
70. E. Schrödinger, Ref. 68, pp. 916–917.
71. E. Schrödinger, Ref. 68, p. 917.
72. E. Schrödinger, Ref. 68, p. 918.
73. E. Schrödinger, Ref. 68, p. 921.
74. E. Schrödinger, Zur Dynamik der elastischen Punktreihe, *Sitz. Ber. Akad. Wiss. (Wien)* **123**, 1679–1696 (1914); reprinted in *Collected Papers 1* (1984), pp. 143–160.
75. A. Einstein, Zum gegenwärtigen Stand des Gravitations problems, *Phys. Z.* **14**, 1249–1266 (1913); presented on September 23, 1913 at the 85th *Naturforscherversammlung* in Vienna.
76. A. Einstein and M. Grossmann, Entwurf einer verallgemeinerten Relativitätstheorie und ein Theorie der Gravitation. I. Physikalischer Teil von A. Einstein. II. Mathematischer Teil von M. Grossmann, *Z. Math. Phys.* **62**, 225–261 (1913).
77. See *Phys. Z.* **15**, 486 (1914).
78. See *Phys. Z.* **15**, 863 (1914).
79. F. K. W. Kohlrausch and E. Schrödinger, Über die weiche ( $\beta$ ) Sekundärstrahlung von  $\gamma$ -Strahlen, *Sitz. Ber. Akad. Wiss. (Wien)* **123**, 1319–1367 (1914); reprinted in *Collected Papers 2* (1984), pp. 32–80.
80. E. Schrödinger, Ref. 1, p. 87.
81. E. Schrödinger, Notiz über den Kapillardruck in Gasblasen, *Ann. Phys. (4)* **46**, 413–418 (1915); reprinted in *Collected Papers 1* (1984), pp. 167–173.
82. E. Schrödinger, Ref. 3.
83. E. Schrödinger, Notes of Lectures, AHQP Microfilm No. 39, Section 2.
84. E. Schrödinger, Zur Akustik der Atmosphäre, *Phys. Z.* **18**, 445–452; (1917) reprinted in *Collected Papers 1* (1984), pp. 3–11.
85. E. Schrödinger, Die Energiekomponenten des Gravitationsfeldes, *Phys. Z.* **19**, 4–7 (1918); reprinted in *Collected Papers 2* (1984), pp. 156–159.
86. E. Schrödinger, Über ein Lösungssystem der allgemein kovarianten Gravitationsgleichungen, *Phys. Z.* **19**, 20–22 (1918); reprinted in *Collected Papers 2* (1984), pp. 160–162.
87. E. Schrödinger, Die Ergebnisse der neueren Forschung über Atom- und Molekularwärmen, *Naturwissenschaften* **5**, 537–543, 561–567 (1917); reprinted in *Collected Papers 1* (1984) pp. 174–187.
88. E. Schrödinger, Der Energieinhalt der Festkörper im Lichte der neueren Forschung, *Phys. Z.* **20**, 420–428, 450–455, 474–480, 497–503, 523–526 (1919); reprinted in *Collected Papers 1* (1984), pp. 216–276.
89. E. Schrödinger, Notebook on “Schwankungsopaleszenz”; this notebook is undated and has been filed on AHQP Microfilm No. 39, Section 4. However, Schrödinger quoted in it a paper of Leonard Ornstein and Frits Zernike in the *Proceedings of the Royal Academy of Sciences*, Amsterdam, which appeared in the second half of 1914. Therefore, one might assume that Schrödinger composed his notes on fluctuation opalescence in late 1914, probably on a furlough from military service (perhaps around Christmas 1914).
90. The two notebooks on “Besprechung der letzten Arbeiten Smoluchowskis,” together containing 51 pages, have been filed on AHQP Microfilm No. 39, Section 5. We do not know whether Schrödinger intended to publish his notes on Smoluchowski, or at least part of them; or whether he used them in lectures.

91. E. Schrödinger, Zur Theorie der Fall- und Steigversuche an Teilchen mit Brownscher Bewegung, *Phys. Z.* **16**, 289–295 (1915); reprinted in *Collected Papers 1* (1984), pp. 166–173.
92. E. Schrödinger, Notiz über die Ordnung der Zufausreihen, *Phys. Z.* **19**, 218–220 (1918); reprinted in *Collected Papers 1* (1984), pp. 214–215.
93. E. Schrödinger, Über ein in der experimentellen Radiumforschung auftretendes Problem der statistischen Dynamik, *Sitz. Ber. Akad. Wiss. (Wien)* **127**, 237–262 (1918); reprinted in *Collected Papers 1* (1984), pp. 188–213.
94. E. Schrödinger, Wahrscheinlichkeitstheoretische Studien, betreffend Schweidler'sche Schwankungen, besonders die Theorie der Meßanordnung, *Sitz. Ber. Akad. Wiss. (Wien)* **128**, 177–273 (1919); reprinted in *Collected Papers 1* (1984), pp. 216–276.
95. The notebooks have been filed on AHQP Microfilm No. 39, Section 3. We conclude that Schrödinger did not start writing the notes on tensor-analytical mechanics before the middle of 1917, probably even later. For the reasons for this conclusion, see Ref. 6, Part 1, p. 220, footnote 454.
96. H. Hertz, *Die Principien der Mechanik (Gesammelte Werke, Volume 3)*, J. A. Barth, Leipzig (1984).
97. F. Paulus, Ergänzungen und Beispiele zur Mechanik von Hertz, *Sitz. Ber. Akad. Wiss. (Wien)* **125**, 835–882 (1916).
98. E. Schrödinger, Manuscript on “Hertz'sche Mechanik und Einstein'sche Gravitationstheorie”: Filed on AHQP Microfilm No. 39, Section 3. For dating, see Ref. 6, Part 1, p. 221, footnote 457.
99. E. Schrödinger, Über Kohärenz in weitgeöffneten Bündeln, *Ann. Phys. (4)* **61**, 69–86, 69 (1920); reprinted in *Collected Papers 2* (1984), pp. 163–180.
100. E. Schrödinger, Theorie der Pigmente von größter Leuchtkraft, *Ann. Phys. (4)* **62**, 603–622 (1920); reprinted in *Collected Papers 4* (1984), pp. 13–32.
101. E. Schrödinger, Versuch einer modellmäßigen Deutung des Terms der scharfen Nebenserien, *Z. Phys.* **4**, 347–354 (1921); reprinted in *Collected Papers 3* (1984), pp. 3–10.
102. E. Fues, Vergleich zwischen den Funkenspektren der Erdalkalien und den Bogenspektren der Alkalien, *Ann. Phys. (4)* **63**, 1–27 (1920).
103. E. Schrödinger, Ref. 101, p. 347.
104. E. Schrödinger, Ref. 101, p. 354.
105. N. Bohr to E. Schrödinger, June 15, 1921; N. Bohr, lecture presented on 18 October 1921 before the Physical and Chemical Society of Copenhagen (Bohr, *Collected Works 4* (1977), pp. 185–256); N. Bohr, 5th Wolfskehl Lecture at Göttingen on June 20, 1922 (Bohr, 1977, p. 494).
106. E. Schrödinger, Über eine bemerkenswerte Eigenschaft der Quantenbahnen eines einzelnen Elektrons, *Z. Phys.* **12**, 13–23 (1922); reprinted in *Collected Papers 1* (1984), pp. 319–323.
107. F. London to E. Schrödinger, December 1926.
108. W. Pauli, Relativitätstheorie, *Encykl. Math. Wiss.* V/2, 539–775 (1926); reprinted in *Collected Scientific Papers 1* (1984), pp. 1–237.
109. E. Schrödinger to W. Pauli, November 7, 1921.
110. H. Weyl, Gravitation und Elektrizität, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. 466–480 (1918); reprinted in *Gesammelte Abhandlungen* (1968), pp. 29–42.
111. H. Weyl, *Raum-Zeit-Materie: Vorlesungen über allgemeine Relativitätstheorie*, Springer, Berlin (1918); English translation (by H. L. Brose): *Space, Time, Matter*, Dover, New York (1952).
112. H. Weyl, Ref. 111, English translation, p. 303.
113. E. Schrödinger, Ref. 106, p. 14.

114. E. Schrödinger, Ref. 106, p. 22.
115. E. Schrödinger, Ref. 106, p. 23.
116. A. Smekal, *Phys. Ber.* **4**, No. 18, 1082–1083 (1922).
117. W. Wilson, The Quantum Theory and Electromagnetic Phenomena, *Proc. R. Soc. London A* **102**, 478–483 (1923).
118. For the modern significance of Schrödinger's introduction of  $\sqrt{-1}$  in Eq. (25), see C. N. Yang: Square Root of Minus One, Complex Phases and Erwin Schrödinger, in *Schrödinger: Centenary of a Polymath*, C. W. Kilmister (Ed.), Cambridge University Press, Cambridge (1987).
119. K. Försterling, Bohrsches Atommodell und Relativitätstheorie, *Z. Phys.* **3**, 404–407 (1920).
120. K. Försterling, Ref. 119, p. 404.
121. W. Pauli, *Phys. Ber.* **2**, No. 9, May 1, 1921, p. 489.
122. E. Schrödinger, Dopplerprinzip und Bohrsche Frequenzbedingung, *Phys. Z.* **23**, 301–303 (1922); reprinted in *Collected Papers* **3** (1984), pp. 11–13.
123. N. Bohr, Über die Anwendung der Quantentheorie auf den Atombau. I. Grundpostulate der Quantentheorie, *Z. Phys.* **13**, 117–165 (1923); reprinted in *Collected Works* **3** (1926), pp. 457–500.
124. E. Schrödinger to W. Pauli, November 8, 1922.
125. E. Schrödinger, Was ist ein Naturgesetz?, *Naturwissenschaften* **17**, 9–11 (1929) (inaugural address delivered on December 9, 1922 at the University of Zurich); reprinted in *Collected Papers* **4** (1984), pp. 295–297.
126. N. Bohr, H. Kramers, and J. C. Slater, The Quantum Theory of Radiation, *Philos. Mag.* (6) **47**, 785–802 (1924).
127. E. Schrödinger to N. Bohr, May 24, 1924.
128. E. Schrödinger, Bohrs neue Strahlungs hypothese und der Energiesatz, *Naturwissenschaften* **12**, 720–724 (1924); reprinted in *Collected Papers* **3** (1984), pp. 26–30.
129. E. Schrödinger, Ref. 128, p. 720.
130. A. Sommerfeld, *Atombau und Spektrallinien*, 4th edn., Friedr. Vieweg & Sohn, Braunschweig (1924).
131. E. Schrödinger to A. Sommerfeld, November 19, 1924; E. Schrödinger, Über die Rotationswärme des Wasserstoffs, *Z. Phys.* **30**, 341–349, 342 (1924); reprinted in *Collected Papers* **1** (1984), pp. 332–380.
132. E. Schrödinger, Die wasserstoffähnlichen Spektren vom Standpunkte der Polarisierbarkeit des Atomrumpfes, *Ann. Phys. (4)* **77**, 43–70 (1925); reprinted in *Collected Papers* **3** (1984), pp. 31–58.
133. E. Schrödinger, Ref. 132, p. 45.
134. D. R. Hartree, Some Relations between the Optical Spectra of Different Atoms of the Same Electron Structure. I. Lithium-like and Sodium-like Atoms, *Proc. R. Soc. London A* **106**, 552–580 (1924).
135. E. Schrödinger to A. Sommerfeld, July 21, 1925.
136. W. Ostwald, Neuere Forschungen zur Farbenlehre, *Phys. Z.* **17**, 322–332, 352–364 (1916); Neuere Fortschritte der Farbenlehre. II, *Phys. Z.* **22**, 88–95, 125–128 (1921).
137. F. K. W. Kohlrausch, Beiträge zur Farbenlehre. I. Farbton und Sättigung der Pigmentfarben, *Phys. Z.* **21**, 396–403 (1920); Beiträge zur Farbenlehre. II. Die Helligkeit der Pigmentfarben, *Phys. Z.* **21**, 423–426 (1920); Beiträge zur Farbenlehre. III. Bemerkungen zur Oswaldschen Theorie der Pigmentfarben, *Phys. Z.* **21**, 473–477 (1920).
138. F. K. W. Kohlrausch, Bemerkungen zur Ostwaldschen sogenannten Farbentheorie, *Phys. Z.* **22**, 402–403 (1921).
139. E. Schrödinger, Ref. 100.

140. H. von Helmholtz, Versuch einer erweiterten Anwendung des Fechner'schen Gesetzes im Farbensystemen, *Wissenschaftliche Abhandlungen* **3**, 407–437 (1895); Versuch, das psychophysische Gesetz auf die Farbenunterschiede trichromatischer Augen anzuwenden, *Wissenschaftliche Abhandlungen* **3**, 438–459 (1895); Kürzeste Linien im Farbensystem, *Wissenschaftliche Abhandlungen* **3**, 460–475 (1895).
141. H. von Helmholtz, Die Störung der Wahrnehmung kleinster Helligkeitsunterschiede durch das Eigenlicht der Netzhaut, *Wissenschaftliche Abhandlungen* **3**, 392–406 (1895).
142. E. Schrödinger, Grundlinien einer Theorie der Farbenmetrik im Tagessehen, (I. Mitteilung), *Ann. Phys. (4)* **63**, 397–426 (1920); reprinted in *Collected Papers* **4** (1984), pp. 33–62.
143. E. Schrödinger, Grundlinien einer Theorie der Farbenmetrik im Tagessehen. (III. Mitteilung), *Ann. Phys. (4)* **63**, 427–456 (1920); reprinted in *Collected Papers* **4** (1984), pp. 63–92.
144. E. Schrödinger, Grundlinien einer Theorie der Farbenmetrik im Tagessehen. (III. Mitteilung). Der Farbenmetrik II. Teil Höhere Farbenmetrik (eigentliche Metrik der Farbe), *Ann. Phys. (4)* **63**, 481–520 (1920); reprinted in *Collected Papers* **4** (1984), pp. 93–132.
145. E. Schrödinger, Farbenmetrik, *Z. Phys.* **1**, 459–466 (1920); reprinted in *Collected Papers* **4** (1984), pp. 133–140.
146. E. Schrödinger, Ref. 144, p. 482.
147. E. Schrödinger, Ref. 144, p. 484.
148. E. Schrödinger, Ref. 144, p. 485.
149. See, e.g., E. Schrödinger to W. Wien, May 28, 1925.
150. E. Schrödinger, Die Gesichtsempfindungen, in *Müller-Pouillet's Lehrbuch der Physik*, 11th edn., Volume 2, 1926, pp. 456–560; reprinted in *Collected Papers* **4** (1984), pp. 183–287.
151. E. Schrödinger, Über den Ursprung der Empfindlichkeitskurven des Auges, *Naturwissenschaften* **12**, 925–929 (1924); reprinted in *Collected Papers* **3** (1984), pp. 148–152.
152. E. Schrödinger, Über die subjektiven Sternfarben und die Qualität der Dämmerungsempfindung, *Naturwissenschaften* **13**, 373–376 (1925); reprinted in *Collected Papers* **4** (1984), pp. 157–160.
153. K. F. Bottlinger, Über die Farbenempfindung beim Temperaturleuchten von iridischen Objekten und von Sternen, *Naturwissenschaften* **13**, 180 (1925).
154. T. Öryng, Über die physikalische Definition der bunten Körperfarben, *Phys. Z.* **26**, 185–187 (1925).
155. E. Schrödinger, Über Farbenmessung, *Phys. Z.* **26**, 349–352 (1925); reprinted in *Collected Papers* **4** (1984), pp. 153–156.
156. E. Schrödinger, Ref. 155, p. 351.
157. E. Schrödinger, Ref. 150, p. 457.
158. E. Schrödinger, Über das Verhältnis der Vierfarben- zur Dreifarbentheorie, *Sitz. Ber. Akad. Wiss. (Wien)* **134**, 471–490 (1925); reprinted in *Collected Papers* **4** (1984), pp. 163–182.
159. E. Schrödinger, Ref. 150, p. 496.
160. E. Schrödinger, Ref. 158, p. 472.
161. E. Schrödinger, Ref. 158, p. 489.
162. P. A. Hanle, *Erwin Schrödinger's Statistical Mechanics, 1912–1925*, Ph.D. thesis, Yale University, New Haven, Connecticut, 1975; The Coming of Age of Erwin Schrödinger: His Quantum Theory of Ideal Gases, *Arch. Hist. Exact Sc.* **17**, 165–192 (1977).
163. G. de Hevesy and F. Paneth, Zur Frage der isotopen Elemente, *Phys. Z.* **15**, 797–805 (1914).
164. K. Fajans, Zur Frage isotopen Elemente, *Phys. Z.* **15**, 935–940, 940 (1914).
165. K. Fajans, Ref. 164, p. 977.

166. E. Schrödinger, Iotopie und Gibbssches Paradoxon, *Z. Phys.* **5**, 163–166 (1921); reprinted in *Collected Papers* **1** (1984), pp. 308–311.
167. E. Schrödinger, Ref. 166, p. 163.
168. J. W. Gibbs, *Elementary Principles of Statistical Mechanics*, Yale University Press, New Haven (1902), Dover, New York (1960).
169. E. Schrödinger, Ref. 166, p. 165.
170. E. Schrödinger, Über die spezifische Wärme fester Körper bei hoher Temperatur und über die Quantelung von Schwingungen endlicher Amplitude, *Z. Phys.* **11**, 170–176 (1922); reprinted in *Collected Papers* **1** (1984), pp. 312–318.
171. M. Born and E. Brody, Über die spezifische Wärme fester Körper bei hohen Temperaturen, *Z. Phys.* **6**, 132–139 (1921); Über die Schwingungen eines mechanischen Systems mit endlicher Amplitude und ihre Quantelung, *Z. Phys.* **6**, 140–152 (1921).
172. E. Schrödinger, Über das thermische Gleichgewicht zwischen Licht- und Schallstrahlen, *Phys. Z.* **25**, 89–94 (1924); reprinted in *Collected Papers* **1**, (1984) pp. 324–329.
173. L. Brillouin, Diffusion de la lumière et des rayons X par un corps transparent homogène—Influence de l'agitation thermique, *Ann. Phys. (9)* **17**, 88–122 (1922).
174. These notes and memoranda have been filed on AHQP Microfilm No. 40, Section 1.
175. A. Smekal, Allgemeine Grundlagen der Quantenstatistik und Quantentheorie, *Encykl. Math. Wiss.* **V/3**, 861–1214 (1926).
176. K. Herzfeld, Kinetische Theorie der Wärme, in *Müller-Pouillet's Lehrbuch der Physik*, 11th edn., *Volume III, Part 2*, Friedr. Vieweg & Sohn, Braunschweig (1925).
177. E. Schrödinger, Spezifische Wärme (theoretischer Teil), in *Handbuch der Physik* (H. Geiger and K. Scheel, eds.), *Volume 10*, Springer, Berlin (1926), pp. 275–320; reprinted in *Collected Papers* **1** (1984), pp. 365–411.
178. E. Schrödinger, Bemerkung zu zwei Arbeiten des Herrn Elemér Császár über Strahlungstheorie und spezifisch Wärmen, *Z. Phys.* **25**, 173–174 (1924); reprinted in *Collected Papers* **1** (1984), pp. 330–331.
179. E. Schrödinger, Über die Rotationswärme des Wasserstoffs, *Z. Phys.* **30**, 341–349 (1924); reprinted in *Collected Papers* **4** (1984), pp. 332–340.
180. We might mention at this point that Schrödinger's approach in 1924 did not finally solve the specific heat problem of molecular hydrogen; one still had to wait for the advent of the new quantum mechanics, and also include the spin of the hydrogen nuclei plus the relative distribution of ortho- and para-hydrogen at different temperatures (the latter was done by D. M. Dennison, The Rotation of Molecules, *Phys. Rev. (2)* **28**, 318–322 (1926); A Note on the Specific Heat of the Hydrogen Molecule, *Proc. R. Soc. London A* **115**, 483–486).
181. E. Schrödinger, Gasentartung und freie Weglänge, *Phys. Z.* **25**, 41–45 (1924); reprinted in *Collected Papers* **1** (1984), pp. 319–323.
182. W. Nernst, Über neuere Probleme der Wärmetheorie, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. 65–90 (1911).
183. F. Reiche, *Die Quantentheorie: Ihr Ursprung und Ihre Entwicklung*, Springer, Berlin (1921); English translation (by H. S. Hatfield and H. L. Brose): *The Quantum Theory*, Methuen, London (1922).
184. F. Reiche, Ref. 183, English translation, p. 79.
185. P. Scherrer, Das ideale Gas als bedingt periodisches System im Sinne der Quantentheorie, *Nachr. Ges. Wiss. Göttingen*, pp. 154–159 (1916).
186. E. Schrödinger, Ref. 181, p. 42.
187. W. K. Keesom, Die chemische Konstante und die Anwendung der Quantentheorie nach der Methode der Eigenschwingungen auf die Zustandsgleichung eines idealen einatomigen Gases, *Phys. Z.* **15**, 695–697 (1914).

188. M. Planck, Zur Theorie des Gesetzes der Energieverteilung im Normalspektrum, *Verh. Dtsch. Phys. Ges. (2)* **2**, 237–245 (1900).
189. M. Planck, Über die absolute Entropie einatomiger Körper, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. 653–667 (1916).
190. P. Ehrenfest and V. Trkal, Deduction of the Dissociation Equilibrium from the Theory of Quanta and a Calculation of the Chemical Constant Based on This, *Proc. Kon. Akad. Wetensch. (Amsterdam)* **23**, 162–163 (1920); Ableitung des Dissoziations-gleichgewichts aus der Quantentheorie und darauf beruhende Berechnung der chemischen Konstanten, *Ann. Phys. (4)* **65**, 609–628 (1921).
191. E. Schrödinger, Bemerkungen über die statistische Entropiefunktion beim dealen Gas, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. 434–441 (1925); reprinted in *Collected Papers I* (1984), pp. 341–348.
192. S. N. Bose, Plancks Gesetz und Lichtquantenhypothese, *Phys. Z.* **11**, 483–488 (1924).
193. A. Einstein, Quantentheorie des einatomigen idealen Gases, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. 261–267 (1924).
194. A. Einstein, Quantentheorie des einatomigen idealen Gases, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. 3–14 (1925).
195. A. Einstein, Zur Quantentheorie des idealen Gases, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. 18–25 (1925).
196. E. Schrödinger, Ref. 191, pp. 434–435.
197. A. Schidlof, Les quanta du rayonnement et la théorie des gaz, *Arch. Sci. Phys. Nat. (5)* **6**, 281–293, 381–392 (1924).
198. E. Schrödinger, Ref. 191, pp. 436–437.
199. E. Schrödinger, Ref. 191, p. 438.
200. E. Schrödinger, Ref. 191, p. 440.
201. E. Schrödinger, Die Energiestufen des idealen einatomigen Gasmodells, *Sitz. Ber. Preuss. Akad. Wiss. (Berlin)*, pp. 23–36 (1926); reprinted in *Collected Papers 3* (1984), pp. 59–72.
202. E. Schrödinger, Zur Einsteinschen Gastheorie, *Phys. Z.* **27**, 95–101 (1926); reprinted in *Collected Papers 3* (1984), pp. 59–72.