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Source: *Archive for History of Exact Sciences*, Vol. 64, No. 2 (March 2010), pp. 113-202

Published by: Springer

Stable URL: <https://www.jstor.org/stable/41342415>

Accessed: 19-05-2020 12:41 UTC

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“Astonishing Successes” and “Bitter Disappointment”: The Specific Heat of Hydrogen in Quantum Theory

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Received: 7 July 2009 / Published online: 13 September 2009
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Abstract The specific heat of hydrogen gas at low temperatures was first measured in 1912 by Arnold Eucken in Walther Nernst’s laboratory in Berlin, and provided one of the earliest experimental supports for the new quantum theory. Even earlier, Nernst had developed a quantum theory of rotating diatomic gas molecules that figured in the discussions at the first Solvay conference in late 1911. Between 1913 and 1925, Albert Einstein, Paul Ehrenfest, Max Planck, Fritz Reiche, and Erwin Schrödinger, among many others, attempted theoretical descriptions of the rotational specific heat of hydrogen, with only limited success. Quantum theory also was central to the study of molecular spectra, where initially it was more successful. Moreover, the two problems interacted in sometimes surprising ways. Not until 1927, following Werner Heisenberg’s discovery of the behavior of indistinguishable particles in modern quantum mechanics, did American theorist David Dennison find a successful theory of the specific heat of hydrogen.

1 Introduction

In 1919, the German theoretical physicist Fritz Reiche, a student of Max Planck and soon to be Professor of Physics in Breslau, published a paper on the quantum theory

Dedicated to the memory of Martin J. Klein.

Communicated by R.H. Stuewer.

This paper was written in cooperation with the joint project in the history of quantum physics sponsored by the *Max-Planck-Institut für Wissenschaftsgeschichte* and the *Fritz-Haber-Institut* in Berlin.

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of the rotational specific heat of hydrogen gas.¹ In one of the earliest confirmations of the new quantum theory, the specific heat of hydrogen at constant volume falls sharply from $5/2 R$ (where R is the gas constant) at room temperature to $3/2 R$ at about 40 K as the rotational degrees of freedom disappear. Reiche's paper was admirable—clear, thorough, and employing the full power of the formalism for describing quantum systems that physicists had developed in the nearly 20 years since Planck's first analysis of black-body radiation late in 1900. And yet Reiche was unsuccessful. None of his models described the specific-heat data accurately, and the ones that came closest required arbitrary and implausible assumptions. The quotation in the title, a description of the state of quantum theory from Reiche's 1921 textbook,² applies equally to his influential efforts to understand the specific heat of hydrogen.

Attempts to understand the specific heats of gases go back to the early days of nineteenth-century kinetic theory. The equipartition theorem³ made specific predictions for gases: each degree of freedom—more precisely, each quadratic term in the energy—should contribute $1/2 RT$ to the average thermal energy per mole and $1/2 R$ to the specific heat at constant volume. It became increasingly clear that this theorem was an inescapable consequence of classical mechanics. Nevertheless, monatomic and diatomic gases stubbornly refused to obey it.

A monatomic gas molecule, for example, has three translational and three rotational degrees of freedom. Its molar specific heat at constant volume should therefore be $3R$. In fact, measurements of the specific heat of mercury vapor, and later of noble gases such as argon and helium, consistently found half that value. Apparently, the rotational degrees of freedom were missing: monatomic gas molecules did not rotate.

Diatomic gases presented an even more difficult case. Physicists pictured diatomic molecules as rotating dumbbells, with three translational and three rotational degrees of freedom—that is, molecules should be free to rotate independently about three coordinate axes (Fig. 1). The combined translational and rotational specific heat at constant volume again should be $3R$ per mole. Moreover, if the two atoms are not rigidly connected but instead joined by a spring, there should be an additional contribution of R , from the kinetic and potential vibrational energies.

Once again, experiments told a different story. The specific heat at constant volume of nitrogen and oxygen is almost exactly $5/2 R$ at room temperature, and that of hydrogen only slightly lower. Apparently, only two rotational degrees of freedom were present; and these molecules did not vibrate. But other diatomic gases such as chlorine had higher specific heats. Worse yet, the specific heats of diatomic gases steadily increase as the temperature rises, suggesting an inexplicable *gradual* onset of additional degrees of freedom. For example, the specific heat at constant volume of

¹ Reiche (1919).

² Reiche (1921, p. 125).

³ The equipartition theorem, whose roots go back to Clausius, Maxwell, and Boltzmann, asserts that each separable quadratic contribution to kinetic or potential energy contributes $1/2 RT$ per mole to the average (thermal) energy, and hence $1/2 R$ to the specific heat. The theory worked better for solids than for gases: if one regards a solid as a collection of three-dimensional harmonic oscillators, equipartition predicted a specific heat of $3R$, in agreement with the widely obeyed Law of Petit and Dulong. It was this law that Einstein had challenged in 1907 with his theory of quantized Planck oscillators.

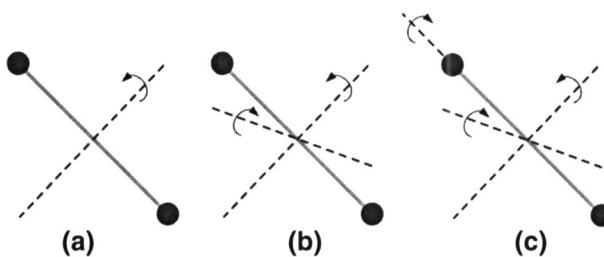


Fig. 1 **a** A rigid rotator with one rotational degree of freedom. It is free to rotate about a single axis that passes through the center of mass, perpendicular to the line joining the two masses. The axis is fixed in space in the direction of the angular momentum. **b** A rigid rotator with two rotational degrees of freedom. It is free to rotate about two mutually perpendicular axes passing through the center of mass. The net result is a rotation about an axis fixed in space in the direction of the angular momentum. **c** A symmetric or gyroscopic rotator with three rotational degrees of freedom. The third rotational degree of freedom corresponds to a rotation about an axis through the two masses; that axis in turn precesses about the fixed direction of the angular momentum

chlorine gas rises from $3R$ (not $5/2 R$) at room temperature to about $7/2 R$ at temperatures over 1,000 K, where it finally becomes constant.⁴ This profound disagreement between theory and experiment did not go unnoticed. James Clerk Maxwell in 1875 called it “the greatest difficulty yet encountered by the molecular theory,” and in 1900, it was one of the two clouds that Lord Kelvin saw hanging over physics. More optimistically, Ludwig Boltzmann argued that atoms and molecules might be “smooth,” so that rotational energy about axes of symmetry could not be changed in collisions or appear in specific heats. This confusing state of affairs still echoes in today’s introductory physics textbooks.⁵

The problem thus remained a mystery when quantum theory appeared on the scene early in the twentieth century. Late in 1900, Max Planck had distributed finite “energy elements” among harmonic oscillators in equilibrium with electromagnetic radiation in order to explain black-body radiation. In 1906, Albert Einstein had treated a solid as a collection of Planck oscillators, and showed that the specific heat should fall to zero at low temperatures. By late in the nineteenth century, physicists and physical chemists were learning to liquefy gases, first air in the late 1870s, then hydrogen in the late 1890s, and finally helium in 1908. As a result, measurements of specific heats at low temperatures became feasible. By 1910, Einstein’s prediction had been conclusively confirmed, and it had become apparent to many theoretical physicists that strange as it might seem, Planck’s quantized oscillators had to be taken seriously.

But how deep did quantum theory go? What other systems should show quantum behavior? How should they be treated? The answers were not obvious. Still, it is hardly surprising to find that the rotating dumbbell was one of the earliest problems to be taken up: perhaps quantum theory could shed light on the inexplicable state of gas theory.

⁴ Partington and Shilling (1924, pp. 226–227), Tabor (1991, pp. 105–108).

⁵ Maxwell (1875), Kelvin (1901), Boltzmann (1896–1898, Vol. 2, Sect. 44), Brush (1976, Chapter 10), Klein (1970, pp. 108–111), Gearhart (1996).

This hope was shortly confirmed, and the quantum solution to the equipartition dilemma soon became a textbook example.⁶ But rotating quantum dumbbells displayed equally pressing difficulties of their own. For the specific heat of hydrogen, qualitative agreement between theory and experiment was quickly achieved. Quantitative agreement was another matter. Reiche's 1919 paper on the specific heat of hydrogen was only the latest in a long series, though it was by far the most comprehensive and complete, and was widely cited for many years. Nor was it to be the last. The first measurements had been published early in 1912. Theoretical studies had begun even earlier. Starting in 1911, and extending through the mid-1920s, such notables as Walther Nernst, Albert Einstein, Paul Ehrenfest, Niels Bohr, and Erwin Schrödinger all made their attempts. In the United States, they were joined by Edwin C. Kemble, Richard C. Tolman, and John H. Van Vleck. The specific heat of hydrogen likewise figured prominently in review articles and textbooks throughout this period. It was a central problem in the "old quantum theory"—the suggestive but ultimately unsuccessful theory that unfolded in the first quarter of the twentieth century.⁷

It should have been a simple problem. Rotating dumbbells—in particular, the rigid rotator and its more complex cousin, the symmetric (or gyroscopic) rotator (see Fig. 1) were then as now textbook problems in classical mechanics.⁸ The quantum rotator, the theoretical underpinning for rotational specific heats, made its first appearance in 1911, and even when extended to two or three degrees of freedom, was far less complex than many other problems treated in the old quantum theory. Generalized to a nonrigid, vibrating rotator, it was also central to the developing discipline of molecular spectra—here, the old quantum theory proved a more reliable guide. The two problems turned out to be interrelated: as the years wore on, a close connection between the specific heat of hydrogen and molecular spectra became increasingly apparent.⁹

Here I tell the story of the rotational specific heat of hydrogen in the old quantum theory and modern quantum mechanics. This story is not as well known as the attempts to describe such problems as the Bohr atom, the helium atom, dispersion, and

⁶ See for example Reiche (1921, Chapter 4, Sect. 1).

⁷ A few of the more prominent texts and review articles include Adams (1920–1923), Eucken (1920a), Reiche (1921), Eucken (1926), Herzfeld (1925), Kemble et al. (1926), Lewis (1918–1924), Partington and Shilling (1924), Smekal (1926), Van Vleck (1926b). For later treatments enthusiastically describing the modern quantum-mechanical solution, see for example Van Vleck (1929), Fowler (1929–1936), and Mayer and Mayer (1940).

⁸ See for example Sommerfeld (1950, Sects. 18, 35), Symon (1960, pp. 384–387). The "rigid rotator" consists of two point masses separated by a fixed distance, and has two rotational degrees of freedom; in textbooks, it is often treated as a spherical pendulum, in which a single reduced mass rotates about the center of mass. The symmetric rotator, with three degrees of freedom, can in addition rotate about a line joining the two masses. See Fig. 1.

⁹ Historical accounts of molecular spectra may be found in Brand (1995), Fujisaki (1982, 1983a,b), Assmus (1991, 1992a,b, 1999), and Cassidy (2007). Occasional and for the most part brief discussions appear in Mehra and Rechenberg (1982–2000). These works contain references to the fairly slim earlier literature. Historians have devoted even less attention to the specific heat of hydrogen. Fujisaki (1983a,b) gives an introduction, and occasional references can be found in Assmus (1991, 1992a,b) and Mehra and Rechenberg (1982–2000, Vol. 1, Section 7, and the index to Vol. 6). Perhaps the most detailed account is in Tomonaga (1997, Chapter 4). See also Needell (1980, pp. 252–262), Kuhn (1978, esp. p. 246), and Klein (1970, pp. 264–270). Many of these references are brief or limited in scope, and some are occasionally misleading.

the anomalous Zeeman effect in the old quantum theory. But it was equally central. Some of the most prominent physicists of the twentieth century, along with a good many who are not well known today, expended enormous effort and ingenuity, and made what seem today like the wildest speculations, in an attempt to solve what turned out to be an intractable problem. No quantitatively accurate solution emerged until David Dennison discovered the modern solution in 1927,¹⁰ two years after Werner Heisenberg had inaugurated modern quantum mechanics. That solution in turn shed light on the nature of indistinguishable particles in quantum mechanics, one of its most surprising and unexpected features. In retrospect, the failure of the old quantum theory to solve this problem is not so surprising, since the modern solution depends centrally on these indistinguishable particles. We will thus see a scientific community coping with a prolonged inability to solve a seemingly elementary problem. Moreover, we will see how the successful solution of a long-standing problem provided additional and persuasive confirmation of modern quantum mechanics—so much so, that Werner Heisenberg’s 1932 Nobel Prize was awarded “for the creation of quantum mechanics, the application of which has, *inter alia*, led to the discovery of the allotropic forms of hydrogen.”¹¹

1.1 Outline

In Sect. 2, I describe the experiments on the specific heat of hydrogen, which along with measurements of the infrared absorption spectrum of HCl provided much of the early experimental support for the new quantum theory. Nernst and Einstein developed the first theory, in which the rotator was not quantized at all, and applied it to the specific heat of hydrogen; I describe their efforts in Sect. 3. Beginning in 1913, a succession of theorists starting with Ehrenfest applied theories of quantized rotators to the specific heat of hydrogen, at first with only one degree of freedom, and then beginning in 1915, with several degrees of freedom. I treat this work in Sects. 4 and 5.

In Sect. 6, I take up molecular spectra in diatomic molecules—a related problem that likewise involved quantized rotating dumbbells. Here, we encounter, in a nearly forgotten episode, Reiche’s and Einstein’s independent discovery of “half-quanta” in the old quantum theory, shortly before Werner Heisenberg introduced them to atomic spectra. The old quantum theory with the addition of half-quanta worked well for molecular spectra; but Sect. 7 describes the subsequent and unsuccessful attempts to apply them to the specific heat of hydrogen. Even the emergence of modern quantum mechanics in 1925–1926 did not at first result in a successful theory of the specific heat of hydrogen, as we shall see in Sect. 8.

Late in 1926, Heisenberg realized for the first time the importance of indistinguishable particles in quantum mechanics and applied these new ideas to the spectrum of helium and to new experimental conundrums in molecular spectra, described in Sect. 9. But even these efforts did not immediately bear fruit. Section 10 shows how Heisenberg’s friend and colleague Friedrich Hund applied Heisenberg’s indistinguish-

¹⁰ Dennison (1927b).

¹¹ http://nobelprize.org/nobel_prizes/lists/1932.html, Cassidy (1992, p. 325).

able particles to a theory of the specific heat of hydrogen early in 1927, in the course of a series of central papers applying quantum mechanics to molecules.

Hund thought he had succeeded. But in Sect. 11, I outline a series of innovative and difficult experiments on the spectrum of molecular hydrogen in the far ultraviolet, that beginning late in 1926 led to an independent measurement of the moment of inertia of the hydrogen molecule. These experiments were the rock on which Hund's theory foundered. Section 12 shows how the American theorist David Dennison, who was in Copenhagen from 1924 through 1926 and had seen the new quantum mechanics emerge at first hand, pulled all of these threads together in mid-1927 and formulated the modern theory. Section 13 shows how Dennison's theory was experimentally confirmed in the late 1920s and early 1930s. I bring the story to an end in Sect. 14.

2 Nernst's heat theorem and the specific heat of hydrogen

Our story begins with Walther Nernst who, shortly after moving from Göttingen to Berlin in 1906, proposed his heat theorem as a solution to the long-standing problem of chemical affinity: how could one predict the equilibrium point of a chemical reaction from thermochemical data?¹² A full discussion of Nernst's heat theorem would take us too far afield. In brief, his theorem predicted that at low temperatures, the specific heats of solids and liquids should be additive.¹³ As Nernst put it in his Yale Silliman Lectures in 1906,

For the specific heats of liquids or solids at the absolute zero, our hypothesis requires that every atom shall have a definite value for the atomic heat, independent of the form, crystallized or liquid (i.e., amorphous), and whether it is in chemical combination with other atoms.

He immediately added that:

Numerous measurements ... have shown ... that the atomic heats in the solid state decrease greatly at low temperatures, but at the present time it is impossible to calculate the limiting value toward which they tend.¹⁴

In a paper submitted at the end of 1906, he noted that specific-heat measurements at temperatures down to the boiling point of hydrogen, or in some cases, that of oxygen, should suffice to test his new heat theorem.¹⁵

¹² Secondary literature on Nernst's heat theorem includes Coffey (2006), Kox (2006), Barkan (1999), Hiebert (1980, 1983), Klein (1965), and Kuhn (1978, esp. Chapter IX). Many of these treatments are fairly brief. For detailed accounts that describe the chemical context, one can do worse than consult Nernst himself; see especially Nernst (1907), the various editions and translations of Nernst (1893–1926), and Nernst (1918).

¹³ This condition cannot apply to reactions in gases, since the number of degrees of freedom and therefore the specific heat can change during the reaction. For one of Nernst's formulations, see Nernst (1893–1926, 6th ed. [1909], p. 695). To be sure, by considering condensed phases and gases in equilibrium, he could also find the equilibrium points of gas reactions.

¹⁴ Nernst (1907, p. 63).

¹⁵ Nernst (1906b).

Thus, as early as 1906, Nernst seems to have looked on the law of Dulong and Petit, which predicts a constant molar specific heat for solids of $3R$, as not beyond challenge. He elaborated on this point in the fifth (1907) edition of his *Theoretical Chemistry*, where it is evident that the specific-heat data he cited (including some of his own preliminary results), although fragmentary and inconclusive, nevertheless showed specific heats of solids at low temperatures becoming smaller than $3R$.¹⁶

Nernst published little during his first few years in Berlin. He seems to have spent much of his time setting up his laboratory and developing the sophisticated apparatus and experimental technique for low-temperature measurements. The development of a vacuum calorimeter that allowed measurements of specific heats over small temperature intervals was especially critical. The year 1910 saw the first in a series of papers giving the specific heats of solids down to liquid-air temperatures (about 75 K), for both compounds and elements.¹⁷

At first, Nernst’s new heat theorem was entirely a matter of chemistry. But at some point he learned, possibly from his Berlin colleague Max Planck, that Albert Einstein, then an examiner in the Swiss Patent Office, had in 1907 published a paper based on Planck’s quantum oscillators predicting that the specific heats of solids should vanish at absolute zero.¹⁸

Nernst reacted with characteristic vigor. By 1909, he was beginning to see that his heat theorem was intimately related to the new quantum theory. He had first referred to Einstein’s work in the sixth (1909) edition of his *Theoretical Chemistry*.¹⁹ And in February of 1910, he observed in one of his first reports on his low-temperature measurements that “one gets the impression that the specific heats are converging to zero, as required by Einstein’s theory.”²⁰ The next month, he descended on Zurich to meet Einstein, then a newly appointed professor at the University of Zurich, and sent a glowing report in a letter to the English physicist Arthur Schuster.²¹ And that summer, Nernst took the leading role in organizing the first Solvay conference to discuss the implications of the emerging quantum theory.²² That conference met in Brussels in late October and early November 1911. Nernst’s report contained pages of specific-heat data, by now extended to liquid-hydrogen temperatures (around 25 K). Einstein’s report included a graph that showed how well Nernst’s measurements supported his own theory, in far more detail than the fragmentary data on diamonds that was all he

¹⁶ Nernst (1893–1926, 5th [1907] ed., p. 177), Klein (1965, p. 176), and Kuhn (1978, p. 213).

¹⁷ See Nernst (1918) and Klein (1965) for full citations; and Eucken (1909), and Nernst (1911a, 1918), for descriptions of the experimental techniques.

¹⁸ Einstein (1907), Klein (1965).

¹⁹ Nernst (1893–1926, 6th [1909] ed., p. 700).

²⁰ Nernst (1910, p. 282), Klein (1965).

²¹ Nernst to Arthur Schuster, 10 March 1910; see Barkan (1999, p. 183) for full citation and an extensive excerpt.

²² See for example Barkan (1999, Chapter 11).

could cite in 1907. He expressed his gratitude, referring to “Nernst, who rescued all the results pertaining to this question from their theoretical limbo....”²³

Although Nernst’s heat theorem initially applied only to solids and liquids, he hoped that it would apply to gases as well. In 1914, in a remarkable anticipation of later theories of quantum gases, he suggested that monatomic gases would show “degenerate” behavior—that is, pressures would become constant and specific heats approach zero as the temperature of the gas approached absolute zero.²⁴

In 1911, however, Nernst’s aims were more limited. In February 1911, well before the Solvay conference, he submitted a paper titled “On the theory of specific heats and the lessons of energy quanta for questions in physical chemistry generally.”²⁵ It shows the close connection he had come to see between his heat theorem and the new quantum theory. Nernst argued that quantum theory might clarify long-standing puzzles with the specific heats of gases. In particular, he predicted that the rotational contribution to the specific heats of diatomic gases should fall to zero at low temperatures, and that:

a falling off of the [rotational energy] at low temperatures will be all the more likely to occur, the smaller the distance between the two atoms and the smaller their masses. In this last respect, hydrogen occupies an exceptional position, and it is in fact the only gas that appears to possess noticeably smaller values [of the specific heat at room temperature]. The determination of the specific heat of hydrogen at low temperatures would therefore be especially interesting.²⁶

2.1 The first experiments: Eucken, Scheel, and Heuse

Where Nernst proposed, his students and assistants disposed. The task of measuring the specific heat of hydrogen fell to Arnold Eucken, who had received his Ph.D. in Nernst’s laboratory in 1906. In 1908, he became one of Nernst’s assistants, and played a central role in designing the vacuum calorimeter that Nernst’s group used to measure the specific heats of solids. Eucken readily adapted these methods to his measurements of the specific heat of hydrogen.²⁷ He measured temperatures using a thin platinum-wire thermometer, another technique that he and Nernst had developed.

Both the experiment and the data reduction were challenging. Eucken crammed about 0.2 moles of hydrogen into a 39-cm³ thin steel container—the pressures were thus very high, on the order of tens of atmospheres. The container was filled through a capillary tube of negligible volume, so that the heat capacity at constant volume was measured directly. However, the heat capacity of the container was not negligible.

²³ In Eucken (1914, p. 337). For Einstein’s talk and related discussions, see also Einstein (1987–2009, Vol. 3, Docs. 25–27). Einstein’s graph was in fact taken from Nernst (1911b).

²⁴ Nernst (1914). Nernst had suggested such a possibility even earlier, in more general terms; see Nernst (1912, p. 1066).

²⁵ Nernst (1911b).

²⁶ Nernst (1911b, p. 271).

²⁷ For more on experimental technique, see Eucken (1909), Nernst (1911a, 1918, Chapter III) Eucken went on to a long and distinguished career; see Dostrovsky (1970), Bartholomé (1950), and Oesper (1950).

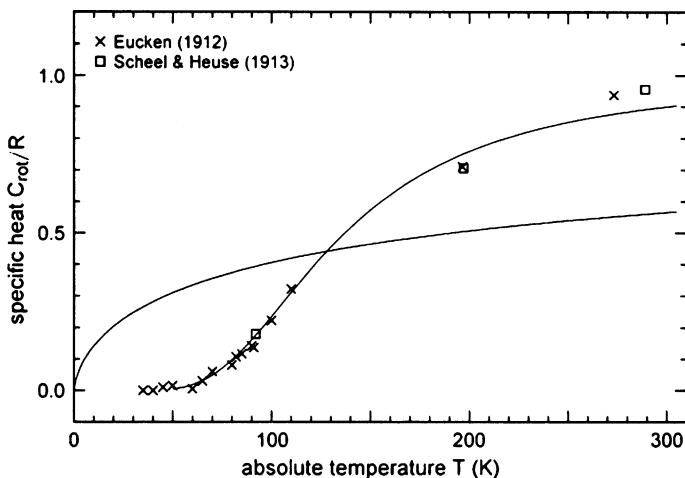


Fig. 2 Data of Eucken (1912) and Scheel and Heuse (1913); note the close agreement at 197 K. I have plotted the rotational part of the specific heat divided by the gas constant R ; the equipartition (room temperature) value of the specific heat for two degrees of freedom equals one on this scale. There was no agreed-upon format for these graphs; this one was as widely used as any. The graphs are my own; the published graphs I discuss are not always of high quality, and a single format makes the interpretation easier. The curves are those of Einstein and Stern (1913). The curve that passes close to the data points was calculated with a zero-point energy. The other curve was calculated with no zero-point energy. I calculated the curves for the specific-heat models here and in subsequent graphs with *Mathematica*

Eucken estimated that at the temperature of liquid air (about 77 K), the filled container had a heat capacity only 20–40% higher than when empty. Only at the lowest temperatures was the heat capacity of the container much smaller than that of the hydrogen gas. Eucken therefore had to measure the heat capacity of his container both filled and empty, and subtract to find the heat capacity of hydrogen. He was well aware of the risk of errors that this procedure entailed, but nevertheless estimated his uncertainty at about 1%, with the largest uncertainties at high temperatures. In addition, since the heat capacity of a real gas depends on its density, Eucken had to reduce his high-pressure measurements to calculate the specific heat of hydrogen at low pressures, where it closely approximated an ideal gas. He used the Berthelot equation of state.

Eucken’s paper appeared in February 1912.²⁸ In what must have been a gratifying result, he found that the specific heat of hydrogen fell from its value of just under $5/2 R$ at room temperature to $3/2 R$, the expected value for a monatomic gas, at around 40 K—see Fig. 2. Nernst’s prediction had been spectacularly confirmed. Remarkably, Eucken attempted to fit his results to Einstein’s 1907 formula for the specific heat of a solid, with only qualitative success. This circumstance will seem less surprising as our story unfolds.

Early in 1913, Karl Scheel and Wilhelm Heuse at the Physikalisch-Technische Reichsanstalt (PTR) added three more points (Fig. 2), in the second of two articles on

²⁸ Eucken (1912). See also Partington and Shilling (1924).

the specific heats of gases published in the *Annalen der Physik*.²⁹ Scheel and Heuse used an entirely different technique, the “method of constant flow,” in which heat was added to gas flowing through a chamber, and the increase in temperature measured. Their first article gave results only for air. The second, which introduced a closed circulation system, gave measurements for several gases. One can readily imagine that Nernst or Planck might have suggested including hydrogen. Without Eucken’s vacuum calorimeter, Scheel and Heuse were limited to the three available temperature baths in which they could immerse their apparatus—water at room temperature, a mixture of carbon dioxide and alcohol at about 197 K, and liquid oxygen at about 90 K. Their experiment measured the specific heat at constant pressure, and so their results had to be reduced to constant volume, after corrections for heat loss and high pressure.

As Fig. 2 shows, and as Scheel and Heuse pointed out, the two sets of measurements were in good agreement. The overlap at 197 K is especially noteworthy, since most of the early theoretical descriptions failed in just this region. In retrospect, both measurements at 197 K are slightly high in comparison to later ones (Figs. 8, 11). These later measurements, however, did not begin to appear until the mid-1920s, and would not have improved matters significantly. For over a decade, the data shown in Fig. 2 provided the only guidance for theorists.

3 Earliest quantum theories of the specific heat of hydrogen

The experiments showed that the rotational degrees of freedom of hydrogen gas are “freezing out” at low temperature. Nernst and Eucken argued that this remarkable turn of events must have its origin in the strange new quantum ideas of Planck and Einstein. In 1911, these ideas were still unknown territory to most physicists. Even such an enthusiast as Nernst could say that: “At the present time, the quantum theory is nothing more than a rule for calculation, and to be sure, as one can well say, of a very strange nature....”³⁰

How should these strange and poorly understood new ideas be applied to a rotating dumbbell, a system quite different from the quantized oscillators of Planck and Einstein? Nernst’s attempt, which he outlined in his February 1911 paper even before Eucken’s data had appeared, was the first in a long line. These theoretical attempts to describe the specific heat of hydrogen can be grouped conveniently into four stages:

- The unquantized quantum rotator: Nernst, Einstein, Otto Stern, and Adriaan Fokker, 1911–1913 (Sect. 3.1);
- Quantized rigid rotators with one rotational degree of freedom: Hendrik Antoon Lorentz, Paul Ehrenfest, Erik Holm, and others, 1911–1916 or so (Sect. 4);
- Quantized rigid (and sometimes vibrating) rotators with two (and occasionally three) rotational degrees of freedom: Planck, Reiche, Bohr, Kemble, and others, 1915–1925 (Sects. 5, 7); and finally,

²⁹ Scheel and Heuse (1912, 1913). Specific heats were important for technology as well as for physics; see Cahan (1989, pp. 197–198), Barkan (1999, pp. 148–150), and Partington and Shilling (1924, pp. 106–110).

³⁰ Nernst (1911b, p. 274).

- Modern quantum mechanics, first formulated in 1925: Van Vleck, Hund, Dennison, and others (Sects. 9, 10, 12).

Nor was the hydrogen molecule the only rotating system under study. In 1912, Niels Bjerrum, a Danish chemist working in Nernst’s laboratory, used a quantized rotator to describe the role of rotations and vibrations in molecular spectra.³¹ During the 1920s, the connection of specific-heat measurements to molecular spectra became increasingly apparent, first with vibration-rotation spectra in diatomic molecules such as HCl, and later with combined electronic, vibrational, and rotational transitions in the spectrum of molecular hydrogen (Sects. 6, 11).

Our story has no one actor and no one approach. For over 15 years, a veritable army of physicists and physical chemists, some eminent, others little known, struggled to understand the specific heat of hydrogen within an evolving theoretical structure that in the end never quite worked. Even the advent of modern quantum mechanics in 1925 did not lead to instant success. It took two more years and a breakthrough in measurements of the molecular spectra of hydrogen before David Dennison could formulate the modern theory in 1927. Dennison’s theory was a second example, following Heisenberg’s success with the spectrum of helium, of the unexpectedly central role of indistinguishable particles and wave-function symmetries in the new theory. The detailed treatments subsequently found in textbooks and review articles, not to mention the sense of relief they display, give further evidence for the prominence of the specific heat of hydrogen in the first three decades of quantum theory. This problem, little-known today, shows in miniature the dilemmas faced by quantum theorists in the first quarter of the twentieth century.

3.1 Nernst and the unquantized quantum rotator

In a 1913 appreciation of Max Planck, Einstein observed that “the thermal energy of every structure depends on the temperature in the same way as that of the resonators in Planck’s theory....”³² The context of that quotation was, to be sure, the specific heat of solids. Nevertheless, it describes perfectly this early effort to understand the specific heat of hydrogen.

In the same February 1911 paper, in which Nernst had proposed measuring the specific heat of hydrogen, he laid out the first theory to explain why the specific heat of a collection of rotating dumbbells should fall off at low temperatures. Surprisingly, from a modern point of view, he did *not* quantize the rotator. Instead, he considered rotating diatomic gas molecules to be in equilibrium with a collection of quantized oscillators, relying heavily on Einstein (1907) treatment of the latter.

In a 1942 obituary, Einstein described Nernst’s scientific style:

Nernst’s standard work, “Theoretical Chemistry,” offers, not only to the student but also to the scholar, an abundance of stimulating ideas; it is theoretically

³¹ Bjerrum (1912). See also Fujisaki (1983a,b), and Assmus (1991, 1992a,b). Assmus has called attention to the central role played by molecular problems in the early years of quantum theory, well before Bohr took up atomic spectra.

³² Einstein (1913, p. 1079).

elementary, but clever, vivid, and full of intimations of manifold interrelations. It truly reflects his intellectual character.³³

The same description might apply to this paper. Nernst was not particularly rigorous. But his physical intuition was extraordinary. As one might expect, he reviewed his recent measurements of the specific heats of solids. Nevertheless, the paper is as much about gases as solids. He began, appropriately for a student of Boltzmann, by pointing out long-standing conflicts between the equipartition theorem and the measured specific heats of gases. For example, the experimental value of C_V for monatomic gases, $3/2 R$, implied the absence of rotational degrees of freedom. Why should such molecules not rotate? “[The] theory furnishes not even a clue....”³⁴ For gases with several atoms, he added, “the contradiction is even more conspicuous.”³⁵ Thus, he noted, for diatomic gases like nitrogen or hydrogen, the value of the specific heat ($5/2 R$) was reasonable,³⁶ but was higher for the halogens; and the specific heats of all diatomic gases *gradually* increased at high temperatures. As Nernst put it: “The theory can account for a new degree of freedom, as in the oscillation of an atom around its equilibrium position, but the gradual emergence of a new degree of freedom is (without new arbitrary assumptions) entirely senseless.”³⁷

To apply quantum theory to rotating gas molecules, Nernst adopted the following strategy:

- He argued that if a solid, thought of as a collection of masses and springs, is in equilibrium with a gas, then the Maxwell–Boltzmann distribution will apply to both.
- He quantized the solid by turning the continuous Maxwell–Boltzmann distribution into a step function, a path that led him to Einstein’s result for the specific heat, “not deductively from … statistical mechanics, but … transparently and visually.”³⁸
- He then extended the argument to gases. Nernst did *not* quantize the rotational motion of a diatomic gas molecule directly, though he did not say so explicitly. Instead, a rotating gas molecule comes into equilibrium by exchanging harmonic-oscillator quanta with a solid. The rotational part of the specific heat of the gas falls off not because the rotational energy is quantized, but because the gas must be in equilibrium with a collection of quantized oscillators.

Nernst’s approach is not easy for modern readers to understand. It is nothing like the tack taken later by quantum theory, and Nernst was not always explicit in spelling out his assumptions. Nevertheless, his was the first attempt to apply quantum theory to

³³ Einstein (1942, p. 196).

³⁴ Nernst (1911b, p. 266).

³⁵ Nernst (1911b, p. 266).

³⁶ Like Boltzmann, Nernst assumed that the degree of freedom corresponding to rotation about a line joining the two atoms did not appear, so that only the two rotational degrees of freedom corresponding to rotations about two axes through the center of mass and perpendicular to that line were present. In modern quantum theory, that degree of freedom does not appear because the small moment of inertia means that the energy of the first excited state is enormously larger than kT .

³⁷ Nernst (1911b, p. 266).

³⁸ Nernst (1911b, p. 267).

diatomic gases; and no less a figure than Albert Einstein adopted a version of it later in 1911. Nernst’s theory is therefore worth examining in more detail.

Like Einstein, Nernst thought of a solid as a collection of three-dimensional harmonic oscillators. In a thoroughly idiosyncratic derivation, he accounted for the three degrees of freedom of a harmonically bound mass point in a three-dimensional solid by projecting its orbit about its equilibrium position onto the three coordinate planes:

[We] can so visualize the motion of a point, that we project its path onto three mutually perpendicular planes, whereby we obtain three “oscillation circles” [*Schwingungskreise*].³⁹

We consider one of three *Schingungskreise*, with which we can describe the motion of an atom about its equilibrium position, and we wish to assume that by the excitation of these oscillations, which we can think of most simply as taking place by the collision with gas molecules, the energy will be absorbed only in definite quanta, and to be sure the oscillation frequency should be directly proportional to this quantum....

[We] will also obtain new points of view for the treatment of the energy of rotational motion, if we seek to apply the theory of energy quanta here, as will be discussed further below.

Nernst continued:

Since we at first disregard the quantum theory and make the assumption that the kinetic energy of the *Schwingungskreise* projected on a plane ... sits in equilibrium with the kinetic energy of the gas molecule projected on the same plane, we arrive at the second consequence, that in both cases the same distribution law obtains.⁴⁰

That law is the Maxwell–Boltzmann distribution. Nernst used the Maxwell–Boltzmann *velocity* distribution to derive a *two-dimensional* speed distribution, which he applied to the plane of a *Schwingungskreis*. He then assumed that “a gas molecule which crashes [*anprallt*] onto a rotating atom is able to take on or withdraw only the energy quantum $\epsilon = h\nu$.⁴¹”

Nernst made a graph of the Maxwell–Boltzmann distribution, not in its usual form but as a graph of the energy of a molecule versus the number of molecules with an energy less than or equal to that value. The result is a monotonically increasing, concave upwards curve, representing, as he said, “a few atoms with a vanishingly small velocity, then a large number approaching the average velocity, and eventually a few atoms with a very large velocity.”⁴²

To quantize the solid, Nernst replaced this curve with a step function, and in a derivation that looked nothing at all like Einstein’s, nevertheless managed to reproduce

³⁹ This word carries a different meaning in contemporary German.

⁴⁰ Nernst (1911b, pp. 266–267).

⁴¹ Nernst (1911b, p. 268).

⁴² Nernst (1911b, p. 268).

Einstein's 1907 result for the energy W of a collection of Planck oscillators. His result for a single *Schwingungskreis*, multiplied by 3, gave

$$W = 3R \frac{\beta\nu}{e^{\frac{\beta\nu}{T}} - 1}. \quad (1)$$

(In Nernst's notation, $\beta = h/k$, where h and k are Planck's and Boltzmann's constants.) A derivative gave Einstein's result for the specific heat of a solid at constant volume. Several pages later, after a discussion of solids, Nernst returned to gases:

We have seen above that a departure from the laws of statistical mechanics emerges if one concerns oneself with the rotation of atoms around an equilibrium position. If we make the certainly obvious generalization of the quantum hypothesis, that energy always will be absorbed only in fixed quanta not only for an oscillation about an equilibrium position, but also for an arbitrary rotation of masses, then we arrive at the wider conclusion that certain contradictions of the old theory may perhaps be clarified. It will, for example, be understandable that a molecule of a monatomic gas may take on no noticeable rotation energy, since by the smallness of the dimension of an individual atom such a rotation could be identified with a *Schwingungskreis* of very high frequency.⁴³

This passage certainly sounds as if Nernst were quantizing the rotators. But it shortly becomes clear that he was doing nothing of the sort. He first took as an approximation that the rotational velocities of all gas molecules will be the same at a given temperature, even though a more complete treatment must assume a Maxwell–Boltzmann distribution.

Nernst then set the *oscillator* frequency in Einstein's specific-heat formula equal to this *rotator* frequency, and in a step Einstein shortly corrected, set the latter proportional to the square root of the absolute temperature, as required by the equipartition law.

In other words, he set $\beta\nu = a\sqrt{T}$ in Eq. (1), and, taking a derivative, found the following elaborate expression for the specific heat per degree of freedom of a rotator:⁴⁴

$$\frac{R}{4} \left[\frac{a}{\sqrt{T}(e^{\frac{a}{\sqrt{T}}} - 1)} + \left(\frac{a}{\sqrt{T}(e^{\frac{a}{\sqrt{T}}} - 1)} \right)^2 e^{\frac{a}{\sqrt{T}}} \right].$$

Nernst showed that for two degrees of freedom, this expression gave the expected value of R at high temperatures. It also predicted that both the rotational energy and specific heat fall off at low temperatures. Nevertheless, although he did not say so explicitly, the rotational frequency is a *continuous* function of temperature, and the rotational energy of a gas molecule is *not* quantized. Later in that year, in a paper written with Frederick Lindemann, Nernst corrected arithmetical errors in his calculation

⁴³ Nernst (1911b, p. 270).

⁴⁴ Remarkably, this obscure formula was still quoted by Partington and Shilling (1924, p. 234) over ten years later.

of the specific heat of oxygen that had been pointed out by Heike Kamerlingh Onnes, and stated with some satisfaction that a similar calculation for hydrogen showed a significant decrease in the specific heat at low temperatures.⁴⁵

3.2 Einstein, Otto Stern, Adriaan Fokker, and the unquantized quantum rotator

The next step came in late October and early November of 1911, when the first Solvay conference brought together about twenty of Europe’s leading physicists to talk about the implications of the new quantum theory.⁴⁶ Nernst’s report repeated his idiosyncratic derivation of Einstein’s result for the specific heat of solids and gave a detailed account of his own specific-heat measurements, but alluded only briefly to gases. Lorentz criticized Nernst’s *Schwingungskreise*, remarking that energy cannot be resolved into components. Lorentz’s comment led to a brief discussion of the difficulties involved in applying quantum theory to systems with several degrees of freedom, the second time this question had come up in the discussions.⁴⁷

Einstein more than made up for Nernst’s neglect of gases. At the end of the first section of his report, expressing the puzzlement he still felt about how to develop a coherent theory of quantum behavior, he observed that “we should consider it a pure stroke of luck” that Planck’s theory, applied to specific heats, leads to a useful result, and added that “totally analogous reasoning yields erroneous results in other cases”—his example here was the kinetic energy of a monatomic gas. He went on to say that:

[We] should greet with skepticism each new application of the method of deducing the thermal properties of matter from [Planck’s] radiation formula....

This fundamental misgiving notwithstanding, one should try to apply this method to the rotary motion of a rigid diatomic molecule about an axis perpendicular to a line connecting the atoms....

I tried to solve this problem, but did not succeed because of mathematical difficulties. The solution would give us a clue to the temperature below which one would expect a departure of the ratio of specific heats from the value 7/5.⁴⁸

Einstein added in a footnote that Nernst had found another approach, and promised to return to it later. He did so in the last section of his report, where he adopted a corrected version of Nernst’s theory. He observed that one need only set the average energy of a Planck oscillator, Eq. (1), to the kinetic energy of a rotator, $\frac{1}{2}J(2\pi\nu)^2$ (where J is the moment of inertia⁴⁹ and ν the rotational frequency of the rotator):

⁴⁵ Nernst and Lindemann (1911, p. 826).

⁴⁶ Barkan (1999, esp. Chapters 10, 11).

⁴⁷ Eucken (1914). See pp. 208–242 for Nernst’s report and the ensuing discussion. Henri Poincaré had earlier asked about systems with several degrees of freedom following the discussion of Planck’s report (p. 99).

⁴⁸ Einstein (1911, p. 339).

⁴⁹ Different authors used different symbols for the moment of inertia. For consistency I use “ J ” (one of the more widely used choices) throughout.

"These two equations contain the relation between E and T we have been looking for; all that remains is to eliminate v ."⁵⁰ He added in a note that Nernst's assumption that v was proportional to the square root of the temperature must be rejected, since it "could only be satisfied if the specific heat were independent of the temperature"—an obvious reference to equipartition. His rotators, like Nernst's, were not quantized—the frequency v is a continuous function of temperature. Einstein was silent, however, on Nernst's conceptual picture; in particular, he did not speak of rotators and oscillators exchanging energy through oscillator quanta.

In the discussion following Einstein's report, Lorentz raised the possibility of quantizing the rotator directly by setting its kinetic energy equal to $n\hbar v$, where n is an integer. The resulting quantized frequencies are proportional to n and the quantized energies to n^2 :

$$v = n \frac{\hbar}{2\pi^2 J}, \quad E = n^2 \frac{\hbar^2}{2\pi^2 J}, \quad (2)$$

as Lorentz pointed out (in slightly different notation). This proposal met with little enthusiasm. Both Paul Langevin and Frederick Lindemann emphasized the qualitative difference between oscillators and rotators—the former has a fixed frequency of oscillation, the latter a variable rotational frequency—and seemed both puzzled and skeptical about how one might apply a theory of quanta to so different a system. Even Lorentz seemed to take his own suggestion with a grain of salt:

But then, this remark is of no great significance. When applying the hypothesis of energy elements, one can confine oneself to systems for which a definite frequency determined by the nature of the process is given in advance.⁵¹

Early in 1913, Einstein elaborated the sketch he had given in Brussels in a joint paper with his assistant Otto Stern.⁵² Stern had completed his Ph.D. degree in physical chemistry with Otto Sackur in Breslau in 1912. Sackur, in turn, had worked briefly with Nernst and had been deeply involved in early efforts to quantize monatomic ideal gases.⁵³ Nevertheless, Stern later recalled that he had learned little quantum theory before he came to work with Einstein in 1912.⁵⁴

The context was notably different from Einstein's brief sketch in Brussels. First, of course, Eucken's data (but not yet those of Scheel and Heuse) had been published. Just as important, Einstein and Stern used the specific heat of hydrogen as a probe to investigate Planck's new zero-point motion.

⁵⁰ Einstein (1911, p. 351).

⁵¹ For the contributions to the discussion by Langevin, Lindemann, and Lorentz, see Eucken (1914, esp. pp. 363–364), reprinted in Einstein (1987–2009, Vol. 3, Doc. 27).

⁵² Einstein and Stern (1913). See also Milonni and Shih (1991), Milonni (1981), Milonni (1994, esp. Chapter 1), Assmus (1991, 1992a), Navarro and Pérez (2006), Mehra and Rechenberg (1982–2000, Vol. 1, pp. 146–148 and 433).

⁵³ Desalvo (1992), Darrigol (1991).

⁵⁴ Thomas S. Kuhn, interview with Otto Stern, May 1962, pp. 3–5, Archives for the History of Quantum Physics (Niels Bohr Library & Archives, American Institute of Physics; Walter Library, University of Minnesota; and elsewhere); hereafter cited as AHQP.

To understand this concept, we must distinguish between Planck’s “first” and “second” quantum theories. Planck’s first theory (as understood by 1913) assumed quantized energies, and energy exchange only through quanta. But in 1910, Lorentz had shown that unreasonably long times would be needed to absorb high-energy quanta.⁵⁵ Planck’s second theory, introduced in 1911, addressed this criticism. It assumed that the oscillators absorbed energy continuously, but emitted energy quanta as they passed through the boundaries of finite phase-space cells of area h . The boundaries of those cells are just $n\hbar\nu$, the energies of the quantum levels in his first theory. Planck’s new theory called attention to the average energy of the oscillators within a given phase-space cell. In the cell bounded by the energies 0 and $\hbar\nu$, that average energy was $\hbar\nu/2$, in some sense a zero-point energy—that is, the average energy of the oscillator did not vanish even at absolute zero.

Einstein and Stern did not adopt Planck’s second theory. But they did explore the implications of a zero-point energy for rotators. A zero-point energy does not affect the specific heat of an oscillator, since its frequency is fixed. But as Einstein and Stern pointed out, a zero-point energy should affect the specific heat of a rotator, since its frequency of rotation depends on the absolute temperature.

Like Nernst, Einstein and Stern assumed that, “for the sake of simplicity,” all rotator frequencies would be the same at a given temperature. And like Einstein in 1911, they equated the kinetic energy of a rotator to the average energy of a resonator with the same frequency, adding a zero-point energy $\hbar\nu/2$:

$$E = \frac{1}{2}J(2\pi\nu)^2 = \frac{\hbar\nu}{e^{\hbar\nu/kT} - 1} + \frac{\hbar\nu}{2}. \quad (3)$$

The specific heat is just the derivative of E with respect to temperature. Einstein and Stern calculated the specific heat of a collection of rotators, both with and without a zero-point energy. The calculations were tedious and the results complicated. For example, for the zero-point case, Einstein and Stern found that the temperature as a function of frequency was given by

$$T = \frac{\hbar}{k} \frac{\nu}{\ln\left(\frac{\hbar}{p\nu-h/2} + 1\right)}, \quad (4)$$

and the specific heat at constant volume by

$$C_V = N_0 2p\nu \frac{\nu}{\ln\left(1 + \frac{kT}{p\nu^2-h^2/4p}\right)}, \quad (5)$$

where $p = 2\pi^2 J$. The equations are similar but a little simpler if the zero-point term is omitted. Eq. (4) is a transcendental equation in the frequency. They either solved it numerically, or (more likely) found by trial and error which frequencies correspond to the desired temperature range, and then used the resulting table of frequencies and

⁵⁵ Lorentz (1910, p. 1251), Needell (1980, Chapter 4).

temperatures to find the specific heat as a function of temperature. These equations do not reduce to a dimensionless form, so that one must choose a particular value for the moment of inertia in Eq. (4) and then see how the specific-heat curve turns out in Eq. (5).

The frequency changes slowly—it varies by only about 25 percent between $T = 0$ and room temperature, and they commented that this slow variation explains why Eucken's fit to Einstein's 1907 harmonic-oscillator specific-heat formula, with a single frequency, worked as well as it did. They also pointed out that the frequency approaches a finite value at $T = 0$ for the zero-point case. These equations reveal clearly that the rotators are not quantized—rotation frequency and energy are continuous (if not at all classical) functions of temperature.⁵⁶

Figure 2 shows their results. The specific heat calculated without a zero-point energy gives an impossible result—it becomes perpendicular to the temperature axis at absolute zero, looking nothing like Eucken's data. By contrast, calculation with a the zero-point energy showed reasonable agreement—Stern and Einstein called it “splendid”—ironically, better than anyone else would achieve for many years.

But how did they interpret their calculation physically? Although their treatment is consistent with Nernst's assumption that resonators and oscillators exchanged energy through oscillator quanta, Einstein and Stern were thinking along very different lines. In a second and almost unrelated section of their paper, they found that a zero-point energy combined with momentum fluctuations led to a derivation of Planck's radiation formula that required no quantum discontinuity.

Energy and momentum fluctuations played a key role in Einstein's thought during these years, not only in Brownian motion but also in quantum theory, where he used fluctuations as a probe into a theory that did not yet exist. In 1909, Einstein had argued for a “wave-particle duality” by considering energy and momentum fluctuations in an electromagnetic field.⁵⁷ For momentum fluctuations, he posited a moving mirror in a radiation field. That mirror experiences a damping force akin to friction; but it also experiences irregular pressure (momentum) fluctuations from the electromagnetic field. To maintain equilibrium, the mean-square velocity of the mirror must remain unchanged at the beginning and end of a short time interval τ . This condition led to a differential equation in the energy density ρ , in which the damping term (right-hand side) is set equal to a momentum fluctuation term (left-hand side):

$$\frac{\overline{\Delta^2}}{\tau} = \frac{3kT}{c} \left(\rho - \frac{v}{3} \frac{d\rho}{dv} \right) f dv. \quad (6)$$

Here, Δ is the momentum fluctuation, ρ the radiation density, and f the area of the mirror. When Einstein substituted Planck's radiation law for the energy density ρ , he found

⁵⁶ The secondary literature can be misleading on this point. Some authors say Einstein and Stern quantized the oscillators, or omit any discussion of how their treatment is to be interpreted. For a notable exception, see Navarro and Pérez (2006). In the older literature, Kuhn (1978) is to my knowledge the only historian who says explicitly that the rotational energy is not quantized, in a brief footnote (note 29, p. 319).

⁵⁷ Einstein (1909a,b), Klein (1964).

$$\frac{\Delta^2}{\tau} = \frac{1}{c} \left(h\nu\rho + \frac{c^3}{8\pi} \frac{\rho^2}{\nu^2} \right) f d\nu. \quad (7)$$

Famously, he argued that the second term on the right was a wave term traceable to Maxwell’s equations, but that the first term was what one would expect for particles—his light quanta of 1905.

A year later, Einstein and his assistant Ludwig Hopf returned to this argument, but from another perspective.⁵⁸ This time, instead of a mirror, they considered a gas of Planck resonators (oscillating dipoles) in equilibrium with electromagnetic radiation. They calculated the momentum fluctuations directly from Maxwell’s equations, and kept the radiation density as an unknown. Einstein’s differential equation now took the following form:

$$\frac{c^2}{8\pi} \frac{\rho^2}{\nu^2} = \frac{3kT}{c} \left(\rho - \frac{\nu}{3} \frac{d\rho}{d\nu} \right). \quad (8)$$

The momentum-fluctuation term on the left-hand side is the same as the wave term in Eq. (7) from 1909; not surprisingly, the solution to this differential equation turns out to be the impossible Rayleigh–Jeans law,

$$\rho = \frac{8\pi\nu^2}{c^3} kT, \quad (9)$$

a result that Ehrenfest later dubbed the “ultraviolet catastrophe.” Einstein and Hopf’s derivation, as they pointed out, did not rely on the possibly dubious application of statistical methods to radiation. In particular, equipartition was used only for the translational motion of the resonator gas, where it seemed most secure. Thus, the Rayleigh–Jeans law followed directly and seemingly inescapably from the momentum fluctuations calculated from Maxwell’s equations.

Fluctuation arguments continued to play a central role in Einstein’s thought for many years—they figured prominently in his *A* and *B* coefficient papers of 1916, for example. They appeared in this 1913 paper as well. Einstein and Stern repeated the Einstein–Hopf calculation of 1910, but this time included a zero-point energy $h\nu$ —not the $h\nu/2$ from their specific-heat calculation—in the otherwise unspecified average resonator energy. Again, they calculated the momentum fluctuation in the resonator using Maxwell’s laws, and set it equal to the damping term to obtain

$$\frac{1}{c} \left(h\nu\rho + \frac{c^2}{8\pi} \frac{\rho^2}{\nu^2} \right) = \frac{3kT}{c} \left(\rho - \frac{\nu}{3} \frac{d\rho}{d\nu} \right). \quad (10)$$

This time, the momentum-fluctuation term on the left-hand side is identical to the one Einstein had found in 1909. As one might expect, the solution to this differential

⁵⁸ Einstein and Hopf (1910).

equation is Planck's radiation law, and the average resonator energy takes on the familiar form

$$E = \frac{h\nu}{e^{h\nu/kT} - 1} + h\nu, \quad (11)$$

with, of course, the zero-point term added on. Einstein and Stern thus had derived both Planck's radiation law and the average resonator energy from Maxwell's equations, with only the additional assumption of a zero-point energy, and, as they said, "without recourse to any kind of discontinuities."⁵⁹

One must conclude that for a time around 1912 and 1913, Einstein had tentatively abandoned the quantization of material systems, and perhaps even his light quanta, in favor of a zero-point energy as the source of all quantum phenomena. To be sure, their calculation was inconsistent; Einstein and Stern had used *different* zero-point energies, $h\nu/2$ and $h\nu$ respectively, to find the specific heat of hydrogen and Planck's radiation law. An attempt to fit the specific heat data using the larger value was unsuccessful. They concluded that:

[The] zero-point energy must be set equal to $h\nu$ in order to arrive at the Planck radiation formula. Future investigations must show whether the discrepancy between this assumption and the assumption underlying the investigation of hydrogen [$h\nu/2$] disappears if the calculation is more rigorous.

They added, with a touch of mystery, that "it seems doubtful that other difficulties can be overcome without the assumption of quanta."⁶⁰

Despite what they had called "splendid agreement" with Eucken's specific-heat data, Einstein soon lost confidence in zero-point motion. At the second Solvay conference in October 1913, he alluded to unspecified "contradictions" in his and Stern's derivation of Planck's radiation law.⁶¹ A month later, in a letter to Ehrenfest in November 1913, he wrote that the zero-point energy is "dead as a doornail" [*maustot*.]⁶² Even earlier, in the summer of 1913, according to a student in Einstein's course in Zurich on the molecular theory of heat, Einstein concluded dismally that "God only knows" how Eucken's data are to be explained.⁶³ But if Einstein had abandoned zero-point motion, he had not given up on the conceptual scheme—an unquantized rotator in equilibrium with a Planck radiation field. Along with a new assistant, Adriaan Fokker, he made one final effort at the end of 1913.

Fluctuations had also figured prominently in Einstein's analysis of Brownian motion. In his first paper on Brownian motion in 1905, Einstein had derived a diffusion equation to calculate the mean-square displacements of particles suspended in

⁵⁹ Einstein and Stern (1913, p. 560)

⁶⁰ Einstein and Stern (1913, pp. 558, 560).

⁶¹ Einstein (1987–2009, Vol. 4, Doc. 22).

⁶² Einstein to Ehrenfest, November 1913, in Einstein (1987–2009, Vol. 5, Doc. 481), see also Einstein to Ludwig Hopf, 2 Nov 1913 (Vol. 5, Doc. 480).

⁶³ Einstein (1987–2009, Vol. 4, pp. 273, 625). The translation quoted from Einstein (1987–2009) is idiomatic; the German reads: "Kein Teufel weiss warum und nach welchem Gesetz."

a viscous fluid, caused by “thermal molecular motion.”⁶⁴ In 1906, he extended that treatment to the calculation of the equilibrium distribution function for any “observable parameter of a physical system.”⁶⁵ His method was to consider an ensemble of systems, and, if we call his observable parameter q , to calculate the number of “system points” crossing a particular value q_0 owing both to thermal fluctuations and to dissipative forces acting on the system. Einstein’s result (which for ease of comparison I write using Fokker’s 1914 notation) was

$$W(q)f(q)\tau + \frac{1}{2}\overline{R^2}\frac{dW}{dq} = 0, \quad (12)$$

where $W(q)$ is the equilibrium distribution function (that is, the number of systems having a value between q and $q + dq$), $f(q) = -dq/dt$ the decrease in q , and $\overline{R^2}$ the mean-square average change in q in the time interval τ owing to random thermal processes. In 1906, Einstein applied this equation only to linear and angular mean-square displacements. He confirmed his 1905 result that the mean-square linear displacement $\overline{x^2}$ is proportional to the time, and found a similar result for mean-square angular displacement. Both were confirmed within the next few years by Jean Perrin.⁶⁶

Adriaan Fokker had completed his Ph.D. degree with Lorentz on the Brownian motion of electrons in an electromagnetic field obeying Planck’s radiation law.⁶⁷ He came to work with Einstein in Zurich in late October or early November, 1913, and immediately began to apply Einstein’s Brownian-motion formalism to the specific heat of hydrogen, taking the parameter $q = L\omega$ as the angular momentum of an electric dipole free to rotate about a fixed axis (where L is the moment of inertia and ω the angular frequency). In this way, he could hope to find a distribution of angular velocities instead of assuming that all angular velocities were the same at a given temperature, as Einstein and Stern had done.

Progress was swift. By early December, Fokker had a result that he described to Lorentz in a letter dated 4 December 1913,⁶⁸ and which he published early in 1914.⁶⁹ Although only Fokker’s name is on the paper, it is evident from both Einstein’s and Fokker’s correspondence,⁷⁰ as well as from Fokker’s acknowledgment to Einstein at the end of the paper, that Einstein took a close interest in this work.

⁶⁴ Einstein (1905). See also editorial notes “Einstein’s Dissertation on the determination of molecular dimensions” and “Einstein on Brownian motion” in Einstein (1987–2009, Vol. 2), Brush (1976, Chapter 15), Renn (2005), and Uffink (2006).

⁶⁵ Einstein (1906, p. 371). See also Nye (1972, p. 117). This paper has received comparatively little attention from historians; but as developed by Fokker, Planck, and others, the approach developed into what is now called the Fokker–Planck equation, a standard tool in nonequilibrium statistical mechanics. See footnote 84, below.

⁶⁶ Perrin (1923), Nye (1972).

⁶⁷ Fokker (1914a).

⁶⁸ Fokker to Lorentz, 4 December 1913, in Einstein (1987–2009, Vol. 5, Doc. 490).

⁶⁹ Fokker (1914b).

⁷⁰ See footnote 68; and Einstein to Paul Ehrenfest, November 1913, in Einstein (1987–2009, Vol. 5, Docs. 481, 484).

In his letter to Lorentz, Fokker wrote down two closely related differential equations, only the second of which appeared in his paper, and described them as generalizations of a method, suggested by Lorentz, that Fokker had used in his dissertation. The first equation,

$$\frac{\partial}{\partial q} [Wf(q)\tau - W\bar{R}] + \frac{1}{2} \frac{\partial^2}{\partial q^2} [W\bar{R^2}] = 0, \quad (13)$$

he said “means that the number [of dipoles] in $(q, q+dq)$ has not changed in the time τ .” The second equation, the only one to appear in print, states that

$$W(q)f(q)\tau - W(q)\bar{R} + \frac{1}{2} \frac{\partial}{\partial q} [W(q)\bar{R^2}] = 0, \quad (14)$$

and “means that an equal number of dipoles pass through the value q in increasing and decreasing direction”—the same condition Einstein had invoked in 1906. As Fokker noted, this equation reduces to Einstein’s 1906 result if $\bar{R} = 0$ and if $\bar{R^2}$ is not a function of q . To both Einstein’s and Fokker’s surprise, the middle term involving \bar{R} was needed if the Maxwell–Boltzmann distribution for the rotators were to result from the Rayleigh–Jeans radiation law. With that result in hand, and with \bar{R} , $\bar{R^2}$, and $f(q)$ all calculated for a rotating electric dipole in a Planck radiation field, Fokker solved for the distribution function $W(q)$, and obtained the unlikely result

$$W = B \text{Exp} \left[-\frac{4\pi^2 LT}{h^2} e^{-\frac{h\omega}{2\pi kT}} + \frac{2\pi L}{h} \omega \right], \quad (15)$$

where B is a constant.

He went on to calculate the average energy and the specific heat—as he remarked in his paper, “the formulas become very complex”—only to discover that his curve for the specific heat approached the y -axis asymptotically, much like Einstein and Stern’s result for the case of no zero-point motion, and thus was entirely incompatible with Eucken’s data. As he said to Lorentz, “This is the result which, of course, I would have liked to be different.”

Einstein was not compelled to take this path. He could easily have followed Lorentz’s lead and quantized the rotators. The approach would have been identical to the one he had followed in 1907 when he used Planck’s abstract quantized oscillators to calculate the fall in the specific heats of solids at low temperatures. He nevertheless chose not to quantize the rotators. His decision shows strikingly the uncertainty that pervaded early quantum theory. Which of Planck’s two theories best described the oscillators? What other systems should show quantum behavior, and what sorts of laws should describe them? As the papers and discussion at the 1911 Solvay conference show, the answers were not obvious to physicists, particularly in the years before Niels Bohr advanced his 1913 theory of the hydrogen atom. This episode shows just how unsettled and uncertain the approach to quantum phenomena could be in those early years, even among its most enthusiastic proponents.

4 Quantized rotators with one degree of freedom

In May 1913, Paul Ehrenfest returned to Lorentz’s suggestion, and put the theory of quantum rotators on the track it would take up to the present day. Ehrenfest first summarized Einstein and Stern’s results, and then said that “a different kind of calculation” leads to the conclusion that “the snuggling up [*anschmiegen*]... to the horizontal axis at $T = 0$ to infinitely high order can be accomplished entirely without the introduction of a zero-point energy.”⁷¹ He did not otherwise draw attention to the very different nature of his calculation, but proceeded, citing Lorentz, to quantize both the rotational frequency and the energy of a rotator through the equations

$$\begin{aligned} \frac{1}{2} J(2\pi\nu)^2 &= n \frac{\hbar\nu}{2}, \quad n = 0, 1, 2, \dots \\ \Rightarrow \varepsilon_n &= \frac{1}{2} J(2\pi\nu)^2 = n^2 \frac{\hbar^2}{8\pi^2 J}. \end{aligned} \quad (16)$$

He commented enigmatically that his factor of 2 in the first equation could be justified “from a very general standpoint”—the first announcement of his adiabatic hypothesis, which was to become a key tool in early quantum theory.⁷²

Ehrenfest used a phase-space analysis (analogous to Planck’s treatment in 1906 for an oscillator) to argue that each energy state was equally probable. He went on to calculate the specific heat, using a then developing and now standard technique, by first writing the equation

$$Q = \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT}, \quad (17)$$

and then showing that the rotational part of the specific heat is given by

$$c_R = 2Nk\sigma^2 \frac{d^2 \ln Q(\sigma)}{d\sigma^2}, \quad \sigma = \frac{\hbar^2}{8\pi^2 J k T}. \quad (18)$$

The factor of 2 was added arbitrarily to take into account the two rotational degrees of freedom of the rigid rotator (see Fig. 1). Before 1915, quantum theorists did not know how to treat problems with more than one degree of freedom. Ehrenfest’s way out of this dilemma had always worked satisfactorily for classical ideal gases, and might have seemed reasonable in 1913. Later on, it would not.

⁷¹ Ehrenfest (1913, pp. 452–453).

⁷² For discussions of this paper and its relation to Ehrenfest’s adiabatic hypothesis, see especially Klein (1970), Needell (1980), Navarro and Pérez (2006), and Pérez (2009).

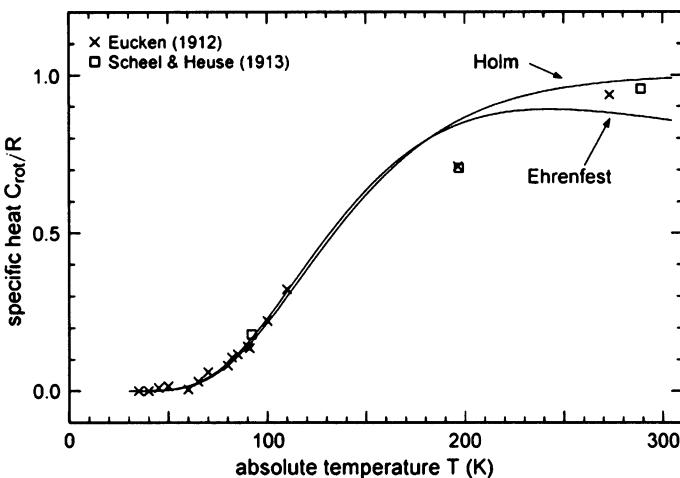


Fig. 3 Specific heat curves of Ehrenfest (1913) and Holm (1913). Ehrenfest's curve goes through a minimum around 500 K before rising slowly to the equipartition value

Q is today called the partition function in English textbooks, and the *Zustandsumme* in German ones.⁷³ Ehrenfest gave it the symbol Q and did not call it anything.⁷⁴ He would have seen it in both Boltzmann (whose student he had been) and Gibbs,⁷⁵ and later, in the calculation of average energy and specific heat of a harmonic oscillator by both Planck and Einstein.⁷⁶ For the harmonic oscillator Q reduces to a geometric series and so is easily summed. No such closed form exists for Ehrenfest's rotator; and for small σ (high temperatures), the sum converges slowly and hence numerical calculations are awkward.⁷⁷ Ehrenfest sidestepped this problem with the use of a special function, the Jacobian theta function, which transforms σ into its inverse.

Ehrenfest's graph is shown in Fig. 3. He chose the moment of inertia so that his curve matched the data at low temperatures.⁷⁸ His curve reaches a peak around 200 K, goes

⁷³ Each term in the partition function is proportional to the probability of finding the system in a particular quantum state, as a function of temperature. It is straightforward to derive thermal quantities, including the specific heat, from appropriate derivatives of the partition function; see for example Reif (1965, Chapters 6, 7).

⁷⁴ Planck, who used the same quantity throughout the 1910s, started using the now-standard symbol Z and the name *Zustandsumme* around 1921, and is often given credit for both. However, Peter Debye (1914, for example p. 27) used both as early as 1914. One still sometimes sees the partition function called Q , particularly in texts written by physical chemists.

⁷⁵ Boltzmann and Gibbs both use this quantity as a normalizing factor in what Boltzmann called a holode, and Gibbs a canonical ensemble. See Boltzmann (1884–1885, Sect. 3), and Gibbs (1902, Chapter IV). Gibbs also discusses its relation to thermal averages.

⁷⁶ Planck (1914a, p. 86), Einstein (1907).

⁷⁷ As temperatures approach the equipartition limit at room temperatures or above, the sum goes over to an integral and is once again fairly easy to calculate. But at intermediate temperatures, the slow convergence of the series made the calculations a challenge, in the days before computers and sophisticated calculators.

⁷⁸ This technique was universally adopted subsequently; different moments of inertia merely shifted the curve along the temperature axis.

through a minimum, and only approaches the equipartition value at temperatures well above 500 K. Similar peaks were to plague theorists for almost fifteen years. Ehrenfest said only a little about it—his emphasis was on showing that he could reproduce the low-temperature behavior without resorting to a zero-point energy. Ehrenfest’s paper led Einstein to suggest calculating the specific heat using *both* quantized energy levels and a zero-point term—it seems that he had not quite given up on zero-point motion after all.⁷⁹

Still later in 1913, Eric Holm, a new Swedish Ph.D. and former mining engineer, applied Ehrenfest’s technique to Planck’s second theory.⁸⁰ In his calculation, Holm replaced quantized energy levels with the average energy of a rotator in a phase-space cell, much as Planck had done in his second theory for resonators. In particular, for a cell bounded by the levels $n - 1$ and n , and assuming that an ensemble of N rotators was uniformly distributed within each cell, he found an average energy $\varepsilon_n = h^2/8\pi^2 J(n^2 - n + \frac{1}{3})$, and remarked on the presence of a zero-point energy for the lowest energy cell. He substituted this result into Ehrenfest’s partition function Q , Eq. (17), and calculated the specific heat. Like Ehrenfest, he multiplied his result by 2 to take into account both degrees of freedom, and used a theta function (albeit a different form) to finesse the slow convergence of the partition series. The result was the graph shown in Fig. 3. As Holm pointed out, the peak is no longer present. Nevertheless, his curve (like Ehrenfest’s) lies well above the data at 200 K, and comes too high at room temperature.

Peter Debye, who had been working independently along the same lines as Ehrenfest, summarized these developments about a year later, in his lectures on quantum theory in Göttingen in the winter term 1914–15.⁸¹ His typed lecture notes devote more than 20 pages to the rigid rotator and its application to both the specific heat of hydrogen and molecular spectra, suggesting the interest that these topics had aroused among quantum theorists. He carefully analyzed Einstein and Stern’s results, simplifying the calculations through well-chosen approximations and series expansions. In the end, though, he pronounced their theory “unsatisfactory.” “By what right can one without further ado set the kinetic energy of a rotating particle equal to the oscillation energy of a resonator...?” Debye also was wary of Ehrenfest’s and Holm’s calculations. He summarized Ehrenfest’s calculation carefully, noting that he had been working along similar lines himself. Nevertheless, he called attention to Ehrenfest’s “hump,” noting that it was not at all in agreement with the data. Holm, he added, had eliminated the unacceptable hump. Nevertheless, he suggested, the recent discovery of sharp rotational peaks in infrared molecular spectra cast doubt on Planck’s second theory. (I shall return to this theme later.) The next step, he concluded, was to seek a better theoretical curve for the specific heat.

⁷⁹ Einstein to Ehrenfest, 8 July 1914, in Einstein (1987–2009, Vol. 8, Doc. 19). Ehrenfest probably never carried out this suggestion. Had he done so, a *Mathematica* calculation shows that his peak would have disappeared.

⁸⁰ Holm (1913), Needell (1980, Chapter 5).

⁸¹ P. Debye, “Lectures on Quantum Theory,” AHQP, microfilm reel 24, pp. 290–313. See also Navarro and Pérez (2006, pp. 218–219).

Thus, by early 1914, Einstein's approach had dropped from sight. Einstein himself had abandoned it, and no one else had adopted it. Two calculations using the partition function had appeared, based respectively on Planck's first and second theories. Both used only one degree of freedom. Each was in qualitative agreement with the specific-heat data, but each failed quantitatively at intermediate and high temperatures. Debye was not the only skeptic. Erwin Schrödinger sounded similarly unimpressed towards the end of a two-part review article on specific heats published in *Die Naturwissenschaften* late in 1917.⁸² An accurate quantum description remained out of reach.

5 Max Planck, Arnold Sommerfeld, and rotators with multiple degrees of freedom

Max Planck was following these developments with considerable interest. In a December 1914 letter to Ehrenfest, he said that “we possess with the problem of the rotating dipoles a highly important gate of entry into the heart [*Innere*] of the quantum hypothesis.” In another letter to Ehrenfest the following March, Planck announced his intention to offer two complementary derivations, one “thermodynamic,” the other “electrodynamical.”⁸³ The former was the derivation that Erik Holm had already published; when Planck came across it in April, he decided to publish only his “electromagnetic” derivation, in which he used a modified version of Fokker's 1914 approach, investigating fluctuations in a rotator in equilibrium with a radiation field. But unlike Fokker, Planck used his second quantum theory and required that Fokker's damping term be nonzero only on the boundaries of the finite phase-space cells. The result of his calculation was identical to Holm's (and his own) “thermodynamic” derivation, much to Planck's satisfaction. Neither this calculation nor Planck's later work with what became known as the Fokker–Planck equation seems to have influenced quantum theory significantly, though as Alan Needell has shown, they did play an important role in the development of Planck's thought.⁸⁴

As it turned out, Planck had bigger fish to fry. Henri Poincaré, at the first Solvay conference in 1911, had asked how one should treat quantum systems with more than one degree of freedom. In a series of three papers submitted in November and December of 1915, Planck provided one answer, which he immediately applied to the rotator and the specific heat of hydrogen.⁸⁵

⁸² Schrödinger (1917).

⁸³ Planck to Ehrenfest, 22 December 1914 and 29 March 1915, AHQP/EHR, microfilm reel 24; see also Needell (1980, Chapter 5, esp. p. 269).

⁸⁴ Planck (1915a). Planck continued to use the Fokker–Planck equation as a probe to investigate the limits of Maxwellian electrodynamics in quantum theory; see Needell (1980) for further discussion. In 1917, Planck (1917a) even published the first proof of the Fokker–Planck equation, which has since become a staple in nonequilibrium statistical mechanics and stochastic theory. See for example Huang (2001, Chapter 18), or Reif (1965, Chapter 15).

⁸⁵ Planck (1915b,c, 1916), Eckert (2008).

In 1906, Planck had shown that his one-dimensional quantum resonators could be described by a “surface” of constant energy in phase space.⁸⁶ The constant energy U of a resonator, given by

$$U = \frac{p^2}{2m} + \frac{1}{2}kq^2, \quad (19)$$

describes an ellipse in this two-dimensional phase space. If these ellipses are specified by Planck’s quantum condition, $U = nh\nu$, then the area of a phase-space cell bounded by successive values of n is just \hbar , Planck’s constant. The size of this cell is proportional to the probability of finding an oscillator in a particular cell (or on a particular boundary). This result justified Planck’s assumption, which had seemed so mysterious to him in 1900, that all complexions (or “microstates”) are equally probable.⁸⁷

In these 1915 papers, Planck extended his treatment to several degrees of freedom. He envisioned a multi-dimensional phase space divided into finite cells by “hypersurfaces” that determine both quantum conditions and the “volume” of finite phase-space cells. These hypersurfaces are in turn related to the constants of the motion (including, of course, the energy), determined by the classical Hamiltonian of the particular system under consideration. The quantum condition is imposed by finding the functional form of each hypersurface g_i , and then setting $g_i = n_i\hbar$, where the n_i are integers. Moreover, the volumes of these phase-space cells are not equal, and so are associated with different probabilities.

Planck stated that this prescription can be applied to either his first or second theory, though, not surprisingly, his examples are mostly drawn from the latter. In his second paper, he distinguished between what he called “coherent” and “incoherent” degrees of freedom. Edwin P. Adams in his 1920 text gave a clear, qualitative description:

In general, each degree of freedom furnishes one hypersurface; but it often happens that two or more degrees of freedom lead to the same hypersurface. Such degrees of freedom, with common hypersurfaces, Planck calls “coherent” degrees of freedom.⁸⁸

Planck himself put it this way:

It is characteristic of the quantum hypothesis, in opposition to the classical theory, that the elementary domains of probability possess a definite form and size; in particular, their boundaries will be defined by certain $(2f - 1)$ dimensional hypersurfaces. Their determination constitutes the most important but also the most difficult part of the problem. The simplest case is the one in which these hypersurfaces are simultaneously the surfaces of constant energy....⁸⁹

⁸⁶ Planck (1906, Sect. 150).

⁸⁷ Gearhart (2002, esp. pp. 196–198).

⁸⁸ Adams (1920, p. 309). Adams (1920–1923) gives the clearest account of Planck’s 1915 theory that I have seen, particularly in the 1920 edition. See also Reiche (1921, p. 94).

⁸⁹ Planck (1915b, p. 351).

For such a system, the volume of the f -dimensional phase space bounded by an energy u_n is given by the single quantum condition,

$$\int\limits_{u=0}^{u=u_n} d\phi_1 \dots d\psi_n = (nh)^f, \quad (20)$$

where the ϕ s and ψ s are, respectively, the generalized coordinates and momenta.

Planck took the rigid rotator and the specific heat of hydrogen as his first example of a system with two coherent degrees of freedom; it is even possible that this problem motivated his new theory. As a first step, he applied his scheme to a rotator with only one degree of freedom, and successfully reproduced Holm's result. He then repeated the calculation for a rigid rotator with two degrees of freedom ($f = 2$). The average energy within a cell turns out to be

$$\bar{u}_n = \frac{\hbar^2}{8\pi^2 J} \left(n^2 + n + \frac{1}{2} \right). \quad (21)$$

The size of the corresponding phase-space cell and the related probability p_n of finding a molecule in that cell are

$$G_n = \{(n+1)^2 - n^2\}\hbar^2 = (2n+1)\hbar^2 \quad \text{and} \quad p_n = 2n+1. \quad (22)$$

Thus, unlike the case for one degree of freedom, the phase-space cells are not all the same size. Therefore, the partition function is not just a sum of Boltzmann factors; rather, each term is "weighted" by the probability appropriate to a given cell.

These "weights" are a characteristic feature of problems with several degrees of freedom. They explain why Ehrenfest's scheme—simply multiplying the one-dimensional result by two, for two rotational degrees of freedom—could not work, and why, therefore, Planck's (and shortly thereafter, Sommerfeld's) generalization was so important. [Compare, in this respect, Eqs. (23) and (17).]

Planck wrote his result in terms of his "thermodynamic potential" (the free energy divided by temperature) which is readily recognized as the logarithm of the partition function:

$$\Psi = Nk \ln \sum_0^{\infty} (2n+1)e^{-(n^2+n+1/2)\sigma}, \quad \sigma = \frac{\hbar^2}{8\pi^2 J k T}. \quad (23)$$

The specific heat is, as before, the second derivative. Planck found the correct limiting behavior (0 and R at low and high temperatures, respectively). But the calculations for intermediate temperatures were even more difficult than those of Ehrenfest and Holm. Planck noted: "Unfortunately, the sum does not reduce so simply to a Jacobean theta function...."⁹⁰ He did not make a graph.

⁹⁰ Planck (1915b, p. 359).

In 1918, Sophie Rotszajn treated the specific heat of hydrogen using Planck’s phase-space theory, with the same continuous energies, in a long paper that also used the rigid rotator to treat paramagnetism. By placing her rotator (here a magnetic dipole) in a magnetic field, she was able to find a solution with “incoherent” degrees of freedom—that is, her hypersurfaces were determined by two constants of the motion, one of which was the energy, and each hypersurface had a separate quantum condition. Her results were notably different from Planck’s.⁹¹

Late in 1915, at the same time that Planck’s papers were appearing, Arnold Sommerfeld introduced a *second* method for treating systems with several degrees of freedom. He postulated that for each degree of freedom, the “phase integral” around a closed path in phase space should be a multiple of Planck’s constant:

$$\oint pdq = nh, \quad (24)$$

where the p and q are, respectively, the generalized momenta and coordinates. This condition picked out the permitted quantum states (in the spirit of Planck’s first theory) from the infinity of classical ones. Although William Wilson in England and Jun Ishiara in Japan had independently made the same suggestion, Sommerfeld showed how to apply it to the fine structure of the hydrogen spectrum, and thus turned it into a fruitful and widely used tool.⁹² Ehrenfest and his student Johannes Burgers explored the implications of Ehrenfest’s adiabatic hypothesis. And Sommerfeld’s former student Paul Epstein and the astronomer Karl Schwarzschild showed how to apply the Hamilton-Jacobi formulation of classical mechanics—hitherto restricted primarily to astronomers, though it has since become a staple of classical mechanics textbooks. The result, by the end of 1916, was a systematic and at first highly successful approach to quantization.⁹³

In brief, one wrote down the Hamiltonian for a system, used Hamilton–Jacobi theory to separate the variables, and then applied the quantization condition, Eq. (24), separately to each degree of freedom. For problems with more than one degree of freedom, it sometimes happens, much as in modern quantum mechanics, that more than one quantum state (or set of quantum numbers) has the same energy. One speaks of “degenerate” quantum states—several different quantum states corresponding to the same energy. It turns out that the number of degenerate states in Sommerfeld’s approach played the same role as the volume of phase space in Planck’s formulation.

⁹¹ Rotszajn (1918). Rotszajn was born in 1873, according to Einstein (1987–2009, Vol. 9, Doc. 131). This paper was her Ph.D. dissertation with Simon Ratnowski in Zurich. I have been unable to learn anything more about her. I discuss her work in more detail in Sect. 5.1. See also footnote 98.

⁹² In his third paper, Planck (1916) alluded to Sommerfeld’s work and showed that his theory of multidimensional phase-space cells could also treat this problem.

⁹³ For discussion and bibliography, including full citations of the work described in this paragraph, see for example Jammer (1966–1989, Chapter 3, Sect. 1). See also Shore (2003); Navarro and Pérez (2006), and Pérez (2009). As Jammer points out, physicists soon showed that Planck’s and Sommerfeld’s quantization conditions were mathematically equivalent. For a detailed treatment, see for example Sommerfeld (1922, 1924, esp. the section “Mathematical Notes and Addenda”), and Goldstein (1959, esp. Chapters. 8, 9).

5.1 Fritz Reiche and the specific heat of hydrogen

In 1919, Fritz Reiche took up the specific heat of hydrogen. Reiche had earned his Ph.D. with Planck in 1907 and went on to spend several years in Breslau working with Otto Lummer, in a less than successful attempt to gain a background in experimental physics. There he met Max Born, who spoke of him with affection and recalled learning a great deal of quantum theory and relativity from him.⁹⁴ Reiche returned to Berlin in 1911, and in 1913 became a *Privatdozent* at the University of Berlin. From 1915 to 1918, he worked as an assistant to Planck—in an interview in 1962, he said that initially he “was not strong enough” to be drafted into the military; later he was classified as “capable of doing work in a bureau.” In 1919–1920, he was an advisor to Fritz Haber’s Physical Chemistry Institute in Berlin, where, he later recalled, he was known as the “little oracle,” in contrast to the “big oracle,” Albert Einstein, with whom he became acquainted during these years.⁹⁵ In 1921, he became Professor in Breslau, and in the same year published a widely read textbook on quantum theory.⁹⁶

Reiche first took up the rotator late in 1917, in an investigation of paramagnetism.⁹⁷ His paper seems to have been motivated by Jan von Weyssenhoff, a student of Simon Ratnowski in Zurich, who in his 1916 Ph.D. dissertation had repeated Erik Holm’s calculation, but had also used a rigid rotator with one degree of freedom to study paramagnetism.⁹⁸ Reiche proposed to use a rotator with two degrees of freedom. Reiche employed Planck’s second theory, but used the Hamilton–Jacobi formalism—the resulting quantized energies also specify Planck’s hypersurfaces in phase space. Following Sommerfeld’s now-standard prescription, Reiche wrote down the familiar Hamiltonian for the rigid rotator, separated it with the Hamilton–Jacobi equations, and then applied Sommerfeld’s quantum condition, Eq. (24), to both of the resulting components of angular momentum.

These developments set the stage for Reiche’s detailed and influential 1919 paper on the specific heat of hydrogen.⁹⁹ He began by summarizing earlier developments: Ehrenfest, Holm, and von Weyssenhoff had calculated the specific heat assuming one degree of freedom. Paul Epstein¹⁰⁰ and Adolf Smekal (in an unpublished work) had done so on the basis of Bohr’s 1913 model of the hydrogen molecule. Finally, Planck and Sophie Rotszajn had done so with Planck’s second theory and two degrees

⁹⁴ Born (1978, pp. 124, 130).

⁹⁵ Thomas S. Kuhn and George E. Uhlenbeck, interview with Fritz Reiche, March and April 1962, AHQP. For the “oracle” story, see the letter of Reiche to Kuhn, 27 July 1962, in the interview file.

⁹⁶ Reiche (1921). For more on Reiche, see Bederson (2005).

⁹⁷ Reiche (1917).

⁹⁸ Weyssenhoff (1916). For more on von Weyssenhoff and Ratnowski, see Mehra and Rechenberg (1982–2000, Vol. 1, p. 431 and Vol. 5, pp. 284–288). The rigid rotator figured in numerous studies of paramagnetism; see for example Holm (1915); Smekal (1918), and Rotszajn (1918). Nevertheless, these theories of paramagnetism do not appear to have attracted much attention. Reiche (1921) does not so much as mention them in his textbook. See also Van Vleck (1932, Chapters I–V; for a negative comment on these early efforts, see p. 303).

⁹⁹ Reiche (1919).

¹⁰⁰ Epstein (1916). Bohr’s model did not allow for a free choice of the moment of inertia, and as a result Epstein’s calculation did not give a satisfactory description.

of freedom, using coherent and incoherent degrees of freedom respectively. Reiche announced that he would do the same calculation for two degrees of freedom, but using Planck’s first theory.

Reiche noted that the motion consisted of a rotation about the center of mass with constant angular velocity, in a plane fixed in space. Therefore, “in spite of the two degrees of freedom, the probability of a state is determined by a single quantity, the energy, and thus we have to deal with a ‘degenerate problem’.” Such degenerate problems, as he pointed out, could present ambiguities.¹⁰¹ Hence, to find the energy of his degenerate rotator, he first referred readers to his 1917 treatment, where he had lifted the degeneracy by treating a rotating magnetic dipole in a magnetic field, and then allowing the field to go to zero; but he also did a second derivation for a “symmetric rotator” (three degrees of freedom; see Fig. 1) in a gravitational field, again taking the appropriate limiting case. Both methods gave the same result for the rotator energy,

$$W_{n_1, n_2} = (n_1 + n_2)^2 \frac{\hbar^2}{8\pi^2 J}, \quad (25)$$

where n_1 and n_2 are integer quantum numbers corresponding to the two degrees of freedom. He next calculated the partition function. Like Ehrenfest, he used the symbol Q but did not give it a name. Assuming that each quantum state was equally probable, he wrote

$$Q = \sum_{n_1} \sum_{n_2} e^{-W_{n_1, n_2}/kT} = \sum_{n_1} \sum_{n_2} e^{-\sigma(n_1 + n_2)^2} \quad \text{where } \sigma = \frac{\hbar^2}{8\pi^2 J k T}. \quad (26)$$

He wrote out the first few terms in this series and showed, assuming positive and negative rotations should be counted separately, that one obtains the single sum

$$Q = \sum_{n=0}^{\infty} (2n+1)e^{-\sigma n^2}. \quad (27)$$

Note that the “weight” in this equation, $2n+1$, represents the number of degenerate states for a given energy, and is the same as Planck’s weight, Eq. (23), derived from the volume of a phase-space cell.

Reiche went on to calculate the specific heat using Eq. (18). As Planck had already discovered, the numerical calculations were not simple. The sum in Eq. (27) does not converge in closed form, and no transformations of the sort Ehrenfest and Holm had used could be found. Reiche responded with brute force. He seems to have taken the sum out to $n = 5$ (either five or six terms, depending on the model),¹⁰² and showed that Eqs. (27) and (18) lead to

$$\frac{c_R}{R} = \sigma^2 \frac{f(x)}{g(x)}, \quad (28)$$

¹⁰¹ Reiche (1919, p. 659). For the ambiguities, see also Van Vleck (1926a, esp. pp. 42, 211).

¹⁰² I can reproduce Reiche’s results in *Mathematica* if I expand Q out to $n = 5$.

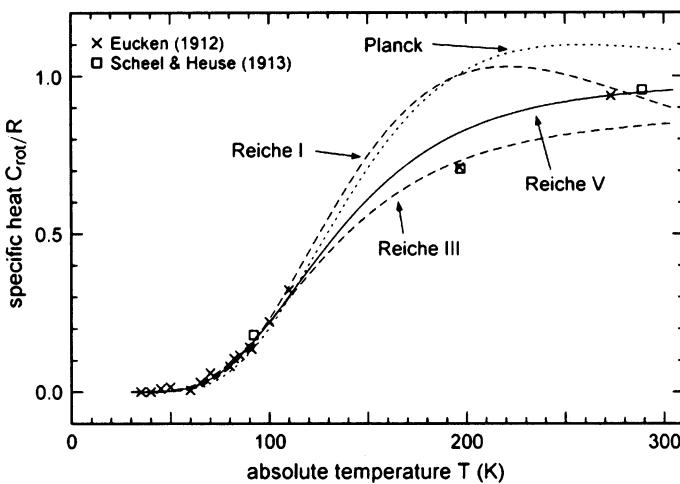


Fig. 4 Specific heat curves of Reiche (1919) and Planck (1915b). Planck's curve (short dashes), which Reiche was the first to publish, approaches the equipartition value from above. Reiche's Curve V (solid) was the best that anyone was able to do for many years, and was widely cited. His Curve I and Curve III are shown with dashed lines

where $x = e^{-\sigma}$. I suspect that this form was chosen for ease of calculation. Even so, the arithmetic is staggering. In Eq. (28), Reiche had to divide a nine-term polynomial $f(x)$ by a 13-term $g(x)$. He then made a table of specific heats versus $1/\sigma$, found a value of the moment of inertia that led to good agreement with the data at the lowest temperatures and, finally, made a table of specific heats versus temperature. He repeated this procedure for five additional cases. Simple mechanical calculators were in use early in the twentieth century, so it is possible that Reiche might have had one available to him. It is equally possible that he had only a slide rule and a table of logarithms. Either way, it was a formidable calculation.

Reiche's results are shown in Fig. 4. The result from the calculation described above, Reiche's Curve I, has a peak higher and broader than Ehrenfest's. Reiche's response was unconditional: "we must throw it out." But what was wrong? Perhaps it was the degeneracy levels—perhaps, for example, one should not count positive and negative rotations as separate states, so that the weight in Eq. (27) became $n + 1$ instead of $2n + 1$. The qualitative shape of the resulting curve (not shown in Fig. 4) was unchanged.

Reiche went on to consider more sweeping special assumptions. "One might therefore make the hypothesis that the rotationless state ... does not exist; that is, one forbids the quantum state $n = n_1 + n_2 = 0$ ".¹⁰³ Zero-point energies thus appeared in the context of Planck's *first* theory, as Reiche pointed out. The resulting graph, his Curve III, is shown in Fig. 4. Encouragingly, the peak was gone. However, the curve came in much too low at room temperatures.¹⁰⁴

¹⁰³ Reiche (1919, p. 674).

¹⁰⁴ Both Curve I and Curve III eventually approach the equipartition value, but only at temperatures considerably above room temperature, contrary to experiment.

Reiche was not finished, however. He next took up an even stranger special case: “Consider a possible if also quite artificial modification. It consists therein, that one forbids not only the quantum state $n = n_1 + n_2 = 0$, but also all states for which $n_2 = 0$.¹⁰⁵ This “quite artificial modification” amounts to an arbitrary restriction on the plane of rotation: Reiche was reduced to introducing a weak vertical gravitational field; his condition then implies that the dumbbell cannot rotate in a plane passing through this vertical direction (or to put it another way, the angular-momentum vector cannot be perpendicular to the vertical).¹⁰⁶ This assumption led to

$$Q = \sum_{n=1}^{\infty} n e^{-n^2\sigma} \quad (29)$$

and to Reiche’s Curve V, also shown in Fig. 4. Widely cited in the ensuing literature, it matched the data well at high and low temperatures, and was the best that anyone was able to do for many years. But as Reiche pointed out in no uncertain terms, it was significantly too high at 200 K, where “the double measurement of Eucken and Scheel-Heuse has a special certainty.”¹⁰⁷

Reiche remembered the discrepancy clearly in his 1962 interview with Thomas S. Kuhn, when he remarked:

And this was the idea, that one tried different ideas for the statistical weights.... One of them was, for instance, that one made the zero state nonexistent. There is always a rotation. ... This also I think eliminated at least the maxima and minima, but it did not give the correct curve anyway....

And so I tried different curves and I think the best still was the curve, number five. But even this was not good. But there was one experimental point terribly below, terribly far off. Nevertheless, at the end of my paper I was careful. I left it open.... Later Eucken was in Breslau for a long time, and I was very much in touch with him. But I’m pretty sure that at that time, I asked him about the reliability of this deviating point And I am pretty sure he said that the point cannot be that far off, it cannot be lifted to such an extent.¹⁰⁸

Reiche’s paper concluded with an analysis of Planck’s second theory. He gave the first published graph of the result Planck had derived in 1915 for coherent degrees of freedom (Fig. 4). It had a peak that was wider and broader than even Reiche’s Curve I. Reiche also pointed out that Sophie Rotszajn’s result, employing incoherent degrees of freedom, was identical to his own Curve V. It is entirely possible that he was led to seek out Eq. (29) in the context of Planck’s first theory after having seen it in her paper. Rotszajn had found a way to use special functions to evaluate her specific heat; but her

¹⁰⁵ Reiche (1919, p. 680).

¹⁰⁶ Reiche (1919, p. 680). gave this explanation at the beginning of Sect. 9, and again in the conclusion. For another clearly stated version of this argument, see Herzfeld (1925, p. 384). The field must be weak to have a negligible effect on the energy of the dumbbell, a point Herzfeld makes explicitly.

¹⁰⁷ Reiche (1919, p. 683).

¹⁰⁸ Reiche, AHQP interview (footnote 95), session 3 (9 May 1962), p. 15.

graph was small and uninformative. She did not plot the data, and less surprisingly, did not plot Planck's curve. Reiche was thus the first to publish careful graphs of both options for Planck's theory, and to compare them to the data.

The upshot was that none of Reiche's curves worked well, and the best of them was the least plausible theoretically, despite a systematic and rigorous treatment that left no possibility unmentioned. Even worse, as he pointed out both in this article and, in a different connection in his 1921 textbook, the models for the specific heat of hydrogen could not answer "one of the most fundamental questions of the whole quantum theory, whether, namely, Planck's first or second theory is correct."¹⁰⁹

Reiche's paper was so thorough, and the physics of the quantum rotator so straightforward, that it was not clear what could be done to improve matters, however unsatisfactory the results. The problem continued to be widely discussed, and other possibilities were eventually pursued. Nevertheless, Max Born, whose 1925 textbook treated most of the unresolved problems in quantum theory at great length, dismissed the specific heat of hydrogen with a few summary paragraphs and a reference to Reiche's 1919 paper.¹¹⁰ A seemingly elementary problem—applying the rigid rotator to the specific heat of hydrogen—still had no satisfactory solution.

5.2 Niels Bohr and the specific heat of hydrogen

Unknown to Reiche, Niels Bohr had tackled the specific heat of hydrogen 3 years earlier, in 1916, in perhaps the most famous unpublished paper in the history of physics—Bohr withdrew it at the last moment after he had seen Sommerfeld's treatment of the fine structure of the hydrogen atom.¹¹¹ Bohr's paper took up a number of themes that were to figure in his later work, among them Ehrenfest's adiabatic hypothesis and early intimations of what became the correspondence principle. But Bohr also analyzed a rigid rotator with two degrees of freedom, and applied it to both molecular spectra and the specific heat of hydrogen.

Bohr began his treatment of the latter by arguing that any periodic system with one degree of freedom should have equally probable quantum states—a generalization based on Planck's 1906 treatment of an oscillator with finite phase-space cells of size h . But this scheme could not be extended to systems with multiple degrees of freedom by treating each degree of freedom separately, as Ehrenfest had done, since the quantization condition "is not satisfied for the different degrees of freedom separately, but for the whole system." Instead, he argued, one must consider that the state of a system with r degrees of freedom will "lie upon a series of $2r - 1$ dimensional surfaces with constant energy" in phase space.¹¹² He could not find the volume of phase space enclosed by such a system of surfaces, but argued that dimensional

¹⁰⁹ Reiche (1921, p. 78; see also p. 125). He made a similar comment in Reiche (1919, p. 658).

¹¹⁰ Born (1925, Sect. 12).

¹¹¹ Bohr (1916). Bohr apparently did circulate copies privately; see the 1920 acknowledgment in Kratzer (1920, p. 292). It eventually appeared in German translation in Bohr (1921). See Bohr's letter to C. W. Oseen, 17 March 1916 for his reasons for withdrawing the paper, in Bohr (1972–1996, Vol. 2, pp. 571–573); see also Pais (1991, p. 184).

¹¹² Bohr (1916, p. 276).

considerations allowed one to conclude that the volume of phase space Q bounded by surfaces corresponding to the quantum number n was

$$Q = C(n\hbar)^r$$

where C is a constant that depends on the particular system. For a rotator its value was one, as he stated without proof.¹¹³

This expression is similar to Planck’s expression for the volume of phase space, Eq. (20). But Bohr’s physical interpretation was markedly different—he was not thinking of finite cells. Instead, he noted that “ordinary statistical mechanics” should apply in the case of large n , and hence in this limit he can show that the probability of finding the rotator in the n th state, corresponding to the quantum number n , is proportional to dQ/dn . Bohr then assumed, in what seems to be an early example of the correspondence principle, that this result holds “not only in the limit but for any value of n .¹¹⁴ Hence the probability, or “weight,” of finding a rotator in the n th state is proportional to

$$n^{r-1} = n \quad \text{for } r = 2.$$

This weight leads directly to Reiche’s Eq. (29); hence Bohr’s result was identical to Reiche’s Curve V! Like Reiche, he remarked on the presence of a zero-point energy and went on to say:

This so-called zero-point energy has here an origin quite distinct from that in Planck’s theory. In the present theory, it arises from the fact, that ... there is no probability of a periodic system of several degrees of freedom being in the state corresponding to $n = 0$.¹¹⁵

Bohr tells us that he had come across Planck’s 1915 theory after his own had been worked out. He observed that their very different predictions for the specific heat of hydrogen might make it possible to distinguish between Planck’s first and second theories, “which differ so widely in their physical meaning.” His brief discussion, however, focused on the contrast between his quantized energy states and the continuous energies found in Planck’s second theory, rather than on the very different character of their phase-space cells and, consequently, the different ways in which they had used a multidimensional phase space for weights and probability calculations. Bohr made graphs of both his specific-heat curve and Planck’s (see Fig. 4), and remarked that his curve agreed much better with the data, though like Reiche he pointed out the discrepancy around 200 K, and raised the possibility of experimental error.

¹¹³ The notation here can be confusing: Bohr used Q for the volume of phase space, not the partition function. He nevertheless calculated the specific heat in much the same way as Ehrenfest had done.

¹¹⁴ Bohr (1916, p. 277) In statistical mechanics, the probability of finding a system in a state n is proportional to the volume of a shell of phase space bounded by n and $n + \delta n$, in this case $(dQ/dn)\delta n$, as Bohr pointed out. Such infinitesimal phase-space cells are typical of (as Bohr put it) “ordinary [i.e., classical] statistical mechanics” but are of course quite different from Planck’s finite cells.

¹¹⁵ Bohr (1916, p. 280).

5.3 Edwin C. Kemble, the specific heat of hydrogen, and molecular spectra

The American physicist Edwin C. Kemble also had taken on the specific heat of hydrogen, in his 1917 Ph.D. dissertation. For Kemble, however, that topic was almost a sidelight—his primary interest lay in the vibration-rotation spectrum of diatomic gases such as HCl. In contrast to Reiche and Bohr, who worked with rigid rotators, Kemble took as central, for both molecular spectra and the specific heat of hydrogen, the picture of a dumbbell that not only rotated about its center of mass, but also vibrated along a line joining the two nuclei. Kemble's work thus gives us an opportunity to examine the close connection that he and other physicists drew between the two problems.¹¹⁶

Kemble began graduate school at Harvard in 1913. He had become interested in quantum theory, in which, he discovered, none of the faculty had much expertise. Nevertheless, with the support of his advisor, Percy W. Bridgman, Kemble pursued a dissertation on the quantum theory of two molecular topics: the specific heat of hydrogen and the vibration-rotation absorption spectrum of diatomic molecules, particularly HCl. In another innovation for Harvard, his dissertation was largely *theoretical*, although the physics faculty did insist that it include an experimental component.¹¹⁷ Kemble had to struggle with a host of difficult theoretical questions without the guidance that European students received from such advisors as Sommerfeld and Born, or that Kemble himself provided for such later students at Harvard as John H. Van Vleck and John C. Slater.

After a short introduction, Kemble began his dissertation by outlining Planck's 1915 theory of multidimensional phase-space cells and its application to the specific heat of hydrogen. He was every bit as thorough as Reiche would be 2 years later. After reviewing Planck's theory, he developed a calculational scheme similar to Reiche's—again, the numerical calculations must have been daunting—and used it to make a graph of Planck's curve, commenting tartly on Planck's failure to do so. Like Reiche and Bohr, Kemble found the high, broad peak shown in Fig. 4. He immediately rejected it, and with it Planck's second theory. He was already disposed to reject Planck's continuous energies. Sharp absorption peaks in infra-red molecular absorption bands¹¹⁸ led Kemble to assume that only discrete, quantized rotational states were possible. Hence Planck's second theory could not be correct.

Kemble, therefore, settled on Planck's first theory, and concluded that allowed states must be limited to the energy hypersurfaces. His calculation for this case was similar to Reiche's, and not surprisingly he reproduced Reiche's Curve I, which he also rejected. But unlike Reiche, Kemble used Planck's finite multidimensional phase-space cells to calculate his weights. Delivery of the *Annalen der Physik* to the United States had been interrupted by the Great War, and as a result, as Kemble later explained, he had not seen Sommerfeld's 1916 *Annalen* paper in which he introduced Eq. (24) to treat

¹¹⁶ Kemble (1917). I discuss these connections briefly in this section and in more detail in Sect. 6.

¹¹⁷ For more on Kemble, see Assmus (1991, 1992a,b, 1999), Holton (1988), and Sopka (1988). See also Thomas S. Kuhn, interview with E. C. Kemble, May 1962, AHQP.

¹¹⁸ Under low resolution, molecular spectra often appear as continuous “bands” rather than discrete lines. It is common to refer to molecular “band spectra” even when higher resolution shows the discrete lines.

problems with several degrees of freedom.¹¹⁹ Planck’s approach, therefore, was the only one available, and Kemble’s use of it was bold and innovative.

Kemble’s next step was to leave out the ground state in the partition function. In this way, he was led—like Reiche and Bohr—to the explicit assumption of a zero-point energy. His choice was reinforced by his work on molecular spectroscopy, which also led him to conclude that rotation-free states in diatomic molecules were forbidden.

Kemble pointed out that a zero-point energy would add an additional complication to the calculations of the specific heat: if energies are on the hyperspace boundaries, and the $n = 0$ case is rejected, which phase-space cell should be chosen to calculate the weight in the partition function? The cell bounding the state from below? From above? Or perhaps an average of the two? Kemble considered all three. The first choice yielded an impossible result. The second and third yielded results identical to Reiche’s Curve III and Curve V, respectively—in Kemble’s dissertation they were labeled Curve C and Curve E.

Unlike Reiche, Kemble found it difficult to decide between them—and here again his interest in molecular spectra came into play. Theories of molecular spectra require a rotator that vibrates along a line connecting the two nuclei. The consequent interaction of vibration and rotation leads to complications; for example:

- The rotator can stretch as it rotates faster. The moment of inertia increases, and hence the spacing of higher rotational energy levels decreases (Eq. 16). Those higher energy levels are thus easier to excite, and can, therefore, lead to higher specific heats at a given temperature. This effect is accentuated if the vibrational potential energy is anharmonic; and Kemble was among the first to show how molecular spectra provide evidence for anharmonic oscillations.
- Vibrational degrees of freedom should contribute to the specific heat of diatomic gases when excitation energies become comparable to kT .

Kemble understood these possibilities clearly from his work on molecular spectra. But their relative importance in 1917 and for some years thereafter, particularly for the specific heat of hydrogen, was far from clear, either theoretically or experimentally. Kemble struggled with both of them. At different times, he thought it possible that either or both of these effects might raise his Curve C (Reiche’s Curve III) closer to the equipartition value at room temperatures. Thus the choice between his Curve C and Curve E was not obvious.

Thus, at the end of his treatment of the specific heat of hydrogen early in his thesis, Kemble said that both curves argued strongly for a zero-point energy. He leaned tentatively toward Curve E, although he pointed out the “considerable error in the experimental value” around 200 K. He also noted the possibility that the excitation of a vibrational degree of freedom starting around 260 K might raise Curve C at higher temperatures, although he thought it unlikely. His summary at the end of his thesis was neutral, though he did comment on the need for better specific-heat data.¹²⁰

¹¹⁹ Kemble (1920, p. 109), Jammer (1966–1989, p. 46).

¹²⁰ Kemble (1917, pp. 23, 121–122). Kemble also commented (p. 116) that the weight leading to curve C seemed most consistent with the absorption spectra of HCl.

However, in an abstract for a paper given at an American Physical Society (APS) meeting later in 1917, Kemble settled firmly on his Curve C (Reiche's Curve III). He assumed "as a first approximation" a harmonic restoring force and argued, in a notable change from his dissertation, that an increase in the moment of inertia of the hydrogen molecule—a possibility not mentioned in his dissertation—is sufficient to bring the upper end of Curve C into agreement with the observations near room temperature. His graph (unlike the one in his thesis, which stops at room temperature) shows a steady increase in the specific heat from room temperature up to about 550 K, and begins to exceed the equipartition result at about 400 K. Kemble did not explain this result. He did state that although his theoretical expression includes a vibrational frequency, it nevertheless treats only the rotational specific heat. He added that vibrational contributions to the specific heat should be seen at temperatures higher than 500 or 600 K. This ambitious attempt did not succeed, though it did provide a starting point for later work.¹²¹

After finishing his Ph.D. in June 1917, Kemble became involved in war work. He returned to Harvard as a faculty member in 1920. His work on the specific heat of hydrogen was not published until 1923, when it appeared in substantially altered form in a joint paper with Van Vleck, Kemble's first Ph.D. student. Kemble and Van Vleck first noted that Kemble's 1917 APS abstract was "marred by an error," and that their purpose was "to present a corrected calculation of the rotational and vibrational specific heat of an elastic model of a diatomic gas molecule." Their treatment was correspondingly complex, and in contrast to Kemble's dissertation and to almost all other calculations of the specific heat of hydrogen, emphasized the behavior of the specific heat at high temperatures, up to about 2,000 K.¹²²

Kemble and Van Vleck began by noting that one could not simply add a vibrational term to the specific heat, since it would not take into account the "expansion of the molecule by centrifugal force." Instead, they introduced an anharmonic restoring force and now using Sommerfeld's formalism, derived a complex and nonseparable equation for the energy of a vibrating rotator as a function of both the rotational and vibrational quantum numbers. This equation used two free parameters to fit the theoretical curve to the data, the rotational frequency at zero vibration,¹²³ and the vibrational frequency at zero rotation. They calculated the specific heat with Reiche's Curve V weights but with their own complex energy expression, noting briefly that Reiche's weights worked best for the rigid rotator. (They also noted pointedly that Kemble had obtained Reiche's results in 1917!) From liquid-hydrogen temperatures to room temperature, their curve is nearly identical to Reiche's Curve V (or Kemble's Curve E). Unlike Reiche, and in contrast to Kemble's dissertation, they remarked briefly that the agreement with the observations is "quite satisfactory."

In fact, their comparison to experimental results strongly emphasized the behavior of the specific heat at high temperatures, where vibrational degrees of freedom should appear, using primarily what they called "less trustworthy" high-temperature data up

¹²¹ Kemble (1918). I was unable to reproduce the calculations summarized in his abstract.

¹²² Kemble and Van Vleck (1923b). See also their abstract for a paper delivered at the 1923 APS Washington meeting, Kemble and Van Vleck (1923a), and the brief discussion in Fellows (1985, esp. pp. 36–42).

¹²³ Essentially the moment of inertia; see Eq. (31).

to about 2,000 K. These data had been collected by Mathias Pier, another of Nernst's assistants, in 1909.¹²⁴ They commented at one point that at the highest temperatures they had carried out their partition series to 13 terms! The numerical computations must have been staggering, particularly given their complex energy expression, and shows the importance they attached to this high-temperature behavior. Van Vleck, many years later, recalled that around 1920 the Harvard physics department did not possess a mechanical calculator, so that he had been forced to borrow one at the business school.¹²⁵

Kemble and Van Vleck's results were widely cited, and Van Vleck used an elastic rotator again in a 1926 review.¹²⁶ Other investigations of the specific heat of hydrogen were, however, almost exclusively confined to rigid rotators, and did not extend higher than room temperature.

6 Vibration-rotation spectra in diatomic molecules

Most of Kemble's thesis, and all of the experimental work it entailed, concerned the infrared absorption spectra of diatomic molecules and their implications for quantum theory. His experimental results, interpreted in the light of his theoretical perspective, reinforced the conclusion from his specific-heat calculations that diatomic molecules could not exist in rotation-free states. It is only one example of the ways in which these two seemingly disparate problems affected one another. A clearer picture of the history of molecular spectra and its relation to the specific heat of hydrogen is thus essential if we are to understand the central importance of these molecular themes for the early history of quantum theory.

6.1 Niels Bjerrum, Eva von Bahr, and vibration-rotation spectra

The theoretical and experimental study of infrared molecular spectra developed roughly in parallel with early quantum theory. Kemble was attracted to this problem by the work of a group of scientists centered in Berlin, where the study of infrared spectra had long been a priority. Their experiments had been essential to Planck's analysis of black-body radiation in 1900.

In 1912, Niels Bjerrum, a Danish chemist working in Nernst's laboratory in Berlin, was the first to take up the connection between quantum theory and molecular spectra, in a paper published in a *Festschrift* for Nernst. Bjerrum began by recalling Paul Drude's conclusion that visible spectra result from electrons, but infrared spectra result from molecular motions that, Bjerrum suggested, include both vibration and rotation. He went on to develop Lord Rayleigh's (1892) argument that if a molecular dipole rotates about an axis perpendicular to its vibrational motion it will emit or absorb radiation not only at its vibrational frequency, call it ν_{vib} , but also about the frequencies $\nu_{\text{vib}} \pm \nu_{\text{rot}}$. According to Bjerrum, the central frequency should be sharp, but the other

¹²⁴ Pier (1909).

¹²⁵ Van Vleck (1964, p. 22).

¹²⁶ Van Vleck (1926b).

two should appear as broad bands, with the rotational velocities distributed according to the Maxwell–Boltzmann law. He went on to suggest that rotational bands should appear at longer wavelengths, corresponding to purely rotational motion, and was able to point to some experimental evidence in support. For example, absorption bands in hydrogen chloride (HCl) in the far infrared might be attributable to rotation, and an absorption band around $3.5\ \mu$ to combined vibration and rotation, though the expected three separate peaks—a sharp line at $3.5\ \mu$, and diffuse ones at 3.4 and $3.6\ \mu$ had not been observed. He concluded that “the experimental evidence supporting the proposed theory is rather weak.”¹²⁷

In the second part of his article, Bjerrum turned to quantum theory. He cited Nernst’s 1911 paper, and observed (incorrectly) that Nernst had quantized both rotational and vibrational motion. Bjerrum went on to quantize the rotational energies and frequencies himself, using the same equations, Eq. (2), that Lorentz had given at the first Solvay conference. Bjerrum could easily have known that result, though he did not cite Lorentz. His conclusion followed at once: “If the rotational frequencies are assumed to vary discontinuously it follows that a band originating from a linear vibration of the rotating molecule must consist of a series of fine lines.”¹²⁸

Bjerrum had supposed in 1912 that these fine lines directly represented the mechanical rotation and vibration frequencies of charged and hence radiating dipoles. Molecular spectroscopists continued this tradition until about 1920, even after Bohr had related atomic spectra to energy *differences* between stable electronic states in 1913.

A year later, Eva von Bahr, a Swedish physicist working in Heinrich Rubens’s laboratory in Berlin, provided spectacular confirmation of Bjerrum’s predictions, as well as strong new evidence for quantum theory.¹²⁹ She called attention to several experimental results, including complex fine structure in the absorption spectrum of water vapor. But her central—and most persuasive—result came from the absorption spectrum of HCl. She first pointed to Wilhelm Burmeister’s spectra, taken with a fluoride prism, that showed the continuous double absorption peaks predicted by Bjerrum. (She seemed uncertain about whether a third central peak was to be expected theoretically, and noted that a narrow line, even if present, might be difficult to detect.) She then displayed her own results, taken with a quartz prism, that showed clear, evenly spaced peaks within the envelopes defined by Burmeister’s “double bands.” The application of Bjerrum’s quantization condition, Eq. (2), led to a moment of inertia for HCl that agreed with a value derived from kinetic theory. It also agreed, as Bjerrum later showed, with a moment of inertia calculated from the separation of the double-band “envelope” using the equipartition law.¹³⁰

¹²⁷ Bjerrum (1912); the quotation is on p. 37.

¹²⁸ Bjerrum (1912, p. 38).

¹²⁹ Bahr (1913, 1914). Eva von Bahr completed her Ph.D. at Uppsala University in Sweden in 1908, and began working in Rubens’s laboratory in Berlin early in 1913. For more on her, see Wennerholm (2009), which contains a great deal of biographical information and analysis, but gives little sense of the importance of her work for early quantum theory.

¹³⁰ Bjerrum (1914). For more extensive accounts and bibliography, see Cassidy (2007), Assmus (1991, 1992a,b), and Fujisaki (1983a,b). For a detailed contemporary account, see Lewis (1916–1924, Vol. III [1919], Chapter IV; and in more detail, 3rd ed. [1924], Chapter IV). See also footnote 148.

6.2 Edwin C. Kemble and vibration-rotation spectra

Kemble’s first two papers, published in 1916, about a year before he completed his doctorate, show a thorough understanding of this literature. He recalled in 1962 that in graduate school he had become interested in quantum theory, especially its implications for infrared molecular spectra. An early calculation suggested to him that the potential energy of molecular oscillators should be anharmonic, and therefore, that harmonics should be emitted or absorbed along with the fundamental frequencies. His first two papers support his recollection. The first summarized Bjerrum’s and von Bahr’s work, and at the same time, corrected one of Bjerrum’s calculations. The second outlined his theoretical argument for an anharmonic potential, and sought possible examples of harmonic bands in the existing literature.¹³¹

The experimental part of Kemble’s dissertation, done together with James Brinsmade, clinched the case.¹³² Brinsmade had developed an infrared spectrometer that, as Kemble put it in his dissertation, was “hastily adapted to the problem in hand at a time when neither Mr. Brinsmade nor the writer knew how far the experiment would be carried.”¹³³ They found double-band first harmonics for CO, HBr, and HCl, and for the last, some of the quantum fine structure. However, the harmonics were not at exactly twice the fundamental frequencies, a discrepancy they were inclined to attribute to an error in the refractive index of their quartz prism.

Just as important, their measurements of the sharp absorption peaks in the fundamental HCl band centered at about $3.5\ \mu$ showed higher resolution and considerably more detail than von Bahr’s. Kemble argued that these peaks directly reflected quantized rotational states, and concluded (like Debye) that Planck’s first theory must therefore be correct.¹³⁴ Their graph (Fig. 5) shows closer spacing of the peaks as the frequency increased, and also displays a prominent gap at the center of the pattern, as if one line were missing (the dashed line shown in the accompanying line drawing).

Kemble attributed the uneven spacing of the lines to an anharmonic elastic force: As the molecule rotated faster, it would stretch, and as a result the frequency at the new equilibrium position would decrease. According to Kemble’s calculations, included in his dissertation but not published until 1920, the peaks should be given by

$$\nu = [\nu_0 - \text{constant} \times m^2 \nu_1^2] \pm m \nu_1 \quad (\text{not Kemble's notation}). \quad (30)$$

Here, ν is the experimentally measured frequency; ν_0 is the frequency of vibration at zero rotation; m is the rotational quantum number; the constant was derived from

¹³¹ Kemble (1916a,b), Kemble, AHQP interview (footnote 117), esp. session 1 (11 May 1962), pp. 6–7; and letter of Kemble to Kuhn, 14 May 1962, on page 14 of the same session. In the first paper, Kemble says that *both* Lorentz and Nernst had quantized the rotator. He also corrected one of Bjerrum’s calculations—Kemble’s lengthy argument led him to Ehrenfest’s quantization condition rather than Lorentz’s. See Assmus (1992b, esp. p. 9).

¹³² Brinsmade and Kemble (1917).

¹³³ Kemble (1917, p. 66).

¹³⁴ Planck (1917b) showed that these peaks were in fact entirely consistent with his second theory. See also the summary in Reiche (1921, pp. 77–78).

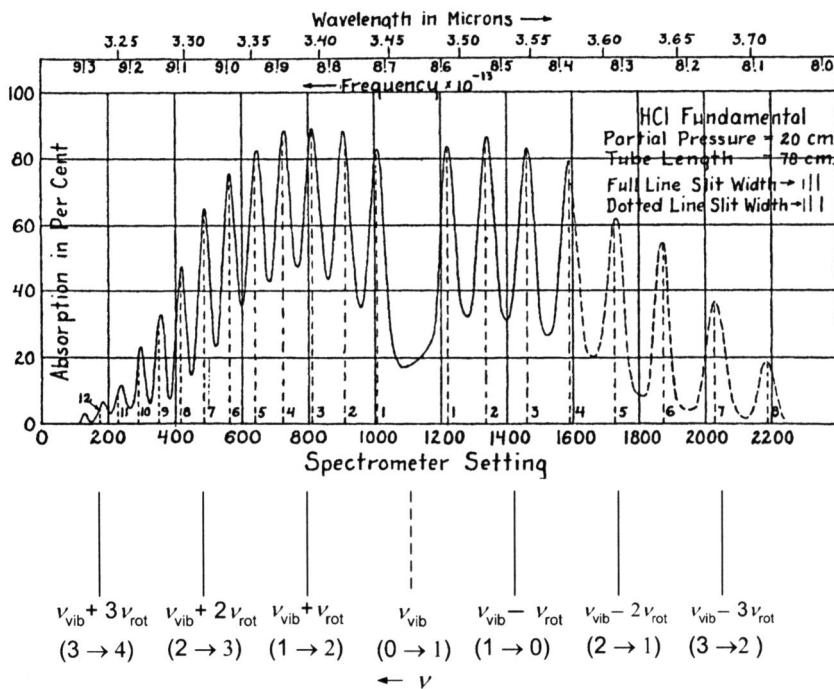


Fig. 5 Brinsmade and Kemble's (1917) vibration-rotation spectrum of HCl. Note the prominent gap at the center. The lines would be evenly spaced, as shown in my accompanying line drawing, if it were not for the effects of an anharmonic potential energy and other corrections. The top labels in the drawing represent Bjerrum's picture in 1912 as well as Kemble's in 1917, in which the lines directly represented mechanical vibration and rotation frequencies. The bottom ones show transitions in absorption, as pictured by Reiche and Kratzer. See Assmus (1992b) for a careful and detailed discussion

the anharmonic force law; and ν_1 is “a certain basic frequency”¹³⁵ identified in Kemble's dissertation with the quantized frequency of rotation corresponding to his and Ehrenfest's quantized energies,

$$\nu_1 = m \frac{\hbar}{4\pi J}. \quad (31)$$

The term in brackets in Eq. (30) thus represented the shift in the frequency of vibration, and the last term the rotational frequency added to or subtracted from the vibrational frequency. They stated that the moment of inertia did not change, by which they seemed to mean that they could describe their data with a single value of ν_1 and hence J ; apparently, the molecule stretched enough to cause an anharmonic decrease in the vibrational frequency, but not enough to change the moment of inertia significantly.¹³⁶ Brinsmade and Kemble found that Eq. (30) predicted the peak spacings satisfactorily.

¹³⁵ Kemble (1920, p. 99).

¹³⁶ Kemble (1917, p. 34).

Indeed, with different theoretical interpretations, similar equations would continue to do good service in succeeding iterations of quantum theory.

The gap was more easily explained. Kemble knew of Bohr’s 1913 theory in 1917; nevertheless, like Bjerrum, he continued to assume that the absorption peaks in HCl represented the mechanical frequencies of vibration and rotation.¹³⁷ In this picture, the gap corresponded to a missing $m = 0$ line, and implied that diatomic molecules could not exist in rotation-free states. This conclusion was reinforced by Kemble’s analysis of the specific heat of hydrogen; there too, the molecules had to rotate. Both Kemble’s dissertation and Brinsmade and Kemble’s paper drew this connection in no uncertain terms. Two separate lines of experimental evidence, strongly conditioned by their theoretical contexts, led Kemble and many others after him to the same inexorable conclusion.¹³⁸

6.3 Elmer Imes and vibration-rotation spectra

In 1919, Elmer Imes, one of the first African-Americans to earn a Ph.D. degree in physics, and a student of Harrison M. Randall at the University of Michigan, extended Brinsmade and Kemble’s measurements on the hydrogen halides.¹³⁹ During a sabbatical leave in 1909–1910, Randall had studied infrared spectroscopy with Friedrich Paschen at the University of Tübingen. On his return to Michigan, he energetically set out to establish a research laboratory in Ann Arbor. At first, under Paschen’s influence, he studied atomic spectra. But Randall tells us that he had been intrigued by Eva von Bahr’s 1913 work on infrared molecular spectra and their connection to the new quantum theory. By 1918, he and his students were beginning to study molecular spectra themselves.¹⁴⁰ Imes described a sophisticated apparatus that used a rock-salt prism to project part of a spectrum onto a grating spectroscope; in this way, he could be sure to separate wavelengths that were integral multiples of one another. He quoted a resolution of 29 Å, which he compared to 70 Å for Kemble and 100 Å for von Bahr. Although his measurements of the fundamental band of HCl represented only a modest improvement over those of Brinsmade and Kemble, he was able to measure the individual lines of the first harmonic in more detail, and resolved for the first time those of HBr and HF. Even more important, he confirmed beyond the possibility of experimental error that the harmonics in HCl and HBr were *not* exact multiples of the fundamental frequencies.

¹³⁷ See Kemble (1918) (the abstract for his 1917 APS paper on the specific heat of hydrogen), which includes a passing reference to “the Bohr theory of atomic structure.” After initial hesitation, Kemble concluded in his 1962 AHQP interview (footnote 117), esp. session 1 (11 May 1962), p. 14, that he had not known of Bohr’s theory this early. His memory apparently led him (and some historians!) astray. It remains unsurprising that he continued to follow Bjerrum’s interpretation, as Assmus has argued in detail.

¹³⁸ See Janssen (2002) for a more general discussion of this theme.

¹³⁹ Imes (1919). This paper, dated April 1918, did not appear until the following year. See also Randall and Imes (1920), an extended abstract for a November 1919 APS meeting. For more on Imes, see Mickens (1998, 1999).

¹⁴⁰ See Nielsen (1960). For Randall’s own accounts, including descriptions of his spectrometer, see Randall (1923a,b, 1954). Imes’s experiment was one of the first two done with the new apparatus.

Were these bands harmonics at all? Imes clearly had his doubts. In their APS meeting abstract, Imes and Randall said bluntly that, “The ‘harmonic’ relationship is therefore not substantiated.” Throughout much of Imes’s paper, the word “harmonics” appears in prominent quotation marks, and there is even one reference to the “so-called harmonics.” Imes used an empirical equation similar to Eq. (30) that was quadratic in the rotational quantum number to describe the uneven spacing of the fine-structure peaks. Not surprisingly, he made no reference to anharmonic forces, and regarded this effect as resulting only from a moment of inertia that increased as the molecule stretched at higher rotational frequencies. He made no mention of Bohr, and took it for granted that the spectral lines represented the mechanical vibration and rotation frequencies.

The application of Bohr’s frequency condition to molecular spectra, so that spectral lines represent *transitions* between nonradiating states, rather than the mechanical vibration and rotation frequencies themselves, took place in stages over several years. Kemble made a start in a 1920 paper in which he both summarized and extended the derivation of his anharmonic term, Eq. (30) from his dissertation: now the expression in brackets, suitably altered, represented the energy *difference* between vibrational states, divided of course by Planck’s constant; the last term, however, remained unchanged, and still represented directly the mechanical rotational frequency of the molecule.¹⁴¹

In this way, Kemble could show that the harmonics need not be exact multiples of the fundamental. Thus, although he did not cite Imes’s paper, he by now agreed that the experimental discrepancy was real, and showed that his new formulation, combining an anharmonic force with Bohr’s frequency condition, could explain the harmonic discrepancy that both he and Imes had measured.

Kemble was not alone in his assumption that his spectral lines represented mechanical frequencies. Karl Schwarzschild¹⁴² and perhaps even Niels Bohr had thought the rotational term in the infrared vibration-rotation spectra represented a mechanical frequency, even though both used term differences to calculate the frequencies of rotational lines elsewhere (Schwarzschild in the visible, Bohr in the far infrared). Even though Bohr calculated frequencies in the far infrared from energy-term differences, he seems to say that von Bahr’s measurements of vibration-rotation spectra in the near infrared directly reflect mechanical rotation frequencies.¹⁴³

¹⁴¹ Kemble (1920). Kemble does not say explicitly that he is treating the two terms differently, but there is no other way to interpret his equations; see for example pp. 99, 101. Adolph Kratzer noticed this difference later in 1920; see Sect. 6.5 below. However, about a year later in a Harvard colloquium, Kemble did describe transitions as arising from changes in rotational, vibrational, and electronic quantum numbers, possibly after seeing Kratzer (1920); see Kemble, notes for Harvard Colloquium, 2 May 1921, AHQP microfilm reel 55.

¹⁴² Schwarzschild (1916, p. 568). Assmus (1991, pp. 93–94 and 1992a, p. 227) first called attention to this aspect of Schwarzschild’s paper.

¹⁴³ Bohr (1916, esp. pp. 261, 267–272 and 281). Bohr’s discussion of von Bahr’s rotation-vibration spectra made no references to term differences, but did make an analogy to the Zeeman effect, which, he argued, is an exception to his term-difference principle. Bohr did calculate frequencies from term differences a page later (pp. 271–272) and even used an intuitively derived selection rule, but made clear his discussion applies to purely rotational spectra in the far infrared, for which, as he said, no experimental evidence yet existed. Such spectra were first measured for HCl by Czerny (1925, 1927). Interestingly, Bohr notes that for a harmonic oscillator, frequencies calculated from term differences, $E_{n+1} - E_n = h\nu$, nevertheless reflect the mechanical frequency of the oscillator; see p. 267. See Darrigol (1992, pp. 90–93), Assmus (1991, pp. 103–105), Assmus (1992a, pp. 228–229).

6.4 Fritz Reiche, vibration-rotation spectra, and the introduction of half-quanta

In 1920, Fritz Reiche and Adolf Kratzer (of whom more later) calculated spectral frequencies from term differences for vibration-rotation spectra more consistently, building on the work of Torsten Heurlinger and Wilhelm Lenz about a year earlier.¹⁴⁴ What came to be called a selection rule, derived from Bohr’s correspondence principle, states that the rotational quantum number changes by $\Delta m = \pm 1$.¹⁴⁵ Using this result together with Eq. (16),¹⁴⁶ it is easy to show that (apart from anharmonic effects) the spectroscopic frequencies are given by

$$\nu = \nu_{\text{vib}} \pm \frac{E_{m+1} - E_m}{h} = \nu_{\text{vib}} \pm \left(m + \frac{1}{2} \right) \frac{h}{4\pi^2 J} \quad m = 0, 1, 2, \dots \quad (32)$$

Here ν_{vib} is the vibrational frequency calculated from the energy difference between vibrational states. The second term represents transitions among rotational states. Thus, in the absorption spectrum of HCl, a molecule goes from the ground state to the first excited vibrational state, and at the same time either absorbs or emits rotational quanta.

At this point, a difficulty emerges: this equation predicts a set of evenly spaced lines (including the dashed line in Fig. 5). By contrast, the data from Kemble and Brinsmade and from Imes clearly show a prominent gap in the center of the pattern, and von Bahr’s data at least suggest a gap. Bjerrum’s (and Kemble’s) original scheme readily explains this gap if rotation-free states are forbidden. This new scheme did not: If one excludes $m = 0$, then two lines are missing, corresponding to rotational transitions $1 \rightarrow 0$ and $0 \rightarrow 1$, and the gap is far too wide. Both Reiche and Kratzer needed a way out.

Reiche submitted his paper for publication in December, 1919, and initially he had only von Bahr’s data with which to work.¹⁴⁷ He first summarized Bjerrum’s theory, and then applied “Bohr’s frequency condition” to both the rigid and the symmetric (or gyroscopic) rotator—he was unable to decide between the two, given, as he said, the imprecision of von Bahr’s data. Reiche derived Eq. (32) for the symmetric rotator, using the solution he had found in his specific heat paper. He eliminated the two lines corresponding to $m = 0$ in Eq. (32) (that is, to the transitions $0 \rightarrow 1$ and $1 \rightarrow 0$), citing his analysis of the specific heat of hydrogen that implied the absence of rotation-free states.

While Reiche’s article was in page proof, however, he had come across Imes’s article in *The Astrophysical Journal*. Imes’s graph of the fundamental band of HCl,

¹⁴⁴ Heurlinger’s work was particularly influential; the American spectroscopist Raymond Birge, for example, in a 1923 letter to Kemble, described Heurlinger’s dissertation as “the most important paper on band spectra ever written” (Birge to Kemble, 4 June 1923, AHQP microfilm reel 50). See Brand (1995, pp. 181–185) and Fujisaki (1983b, pp. 69–73) for discussion and bibliography.

¹⁴⁵ Adalbert Rubinowicz, a student of Sommerfeld, gave an alternative derivation; see for example Darrigol (1992, Chapter 6).

¹⁴⁶ The rotational quantum number n in Eq. (16) is the same one as m here.

¹⁴⁷ Reiche (1920).

much like Kemble's (Fig. 5) but unlike von Bahr's,¹⁴⁸ showed a central gap clearly and unambiguously. The result was a strongly written postscript, in which Reiche said that Eq. (32) could not possibly be correct: without the two omitted $m = 0$ lines, the central gap was far too wide; and with them, there was no gap. Reiche added that he had discussed this problem frequently with Einstein, who had pointed to a possibility for removing the contradiction.¹⁴⁹ If one replaced Eq. (16) with

$$E_m = \left(m + \frac{1}{2}\right)^2 \frac{\hbar^2}{8\pi^2 J} \quad (33)$$

then Eq. (32) became

$$\nu = \nu_{\text{vib}} \pm \frac{E_{m+1} - E_m}{h} = \nu_{\text{vib}} \pm (m + 1) \frac{\hbar}{4\pi^2 J} \quad m = 0, 1, 2, \dots \quad (34)$$

in agreement, as Reiche said, with Imes's observations—this equation gives a gap of appropriate size, with evenly spaced lines on either side. Einstein's suggestion, as far as I know, represents the first introduction of “half-quanta” into quantum theory—“a very remarkable business,” as Einstein called it in a letter to Paul Ehrenfest later that year. In a letter to Fritz Haber, Einstein also noted that both the specific heat of hydrogen and the HCl spectrum imply a zero-point energy of rotation.¹⁵⁰

Arnold Eucken treated the same theme in a long review article on the application of quantum theory to molecular rotation submitted for publication in January 1920.¹⁵¹ He too inferred the absence of rotation-free states from both the specific heat of hydrogen and molecular spectra. He independently derived the Bohr frequency condition, Eq. (32), though in a note he said that he had since discovered the same result in a publication by Lenz. Like Reiche, he had come across Imes's results for HCl while his article was in proof. In a puzzled-sounding footnote, in the midst of a section arguing for Bohr's frequency condition, he said with apparent surprise that Imes's data were better described by Bjerrum's picture. Unlike Reiche, he offered no resolution, though he would shortly do so.

¹⁴⁸ Assmus (1992a) and Brand (1995, p. 172) reproduce von Bahr's graph.

¹⁴⁹ See also Reiche's description in his AHQP interview (footnote 95), session 2 (4 April 1962), p. 9 and session 3 (9 May 1962), pp. 16–17. Einstein and Reiche had both been in Berlin for some years, and seem to have first met in 1914; see the letter of Einstein to Reiche, 18 July 1914 in Einstein (1987–2009, Vol. 8, Doc. 21). They had gotten to know each other fairly well; in a 1990 address, Reiche's son Hans describes frequent visits from Einstein, to which he and his sister always looked forward. See Hans Reiche, “My recollections of Einstein,” in the Reiche papers, Niels Bohr Library, American Institute of Physics, College Park, MD, Series VI, Box 13.

¹⁵⁰ Einstein to Paul Ehrenfest, 1 March 1920, in Einstein (1987–2009, Vol. 9, Doc. 335). See also Einstein to Ehrenfest, 30 July 1920 and Einstein to Fritz Haber, 6 October 1920, in Einstein (1987–2009, Vol. 10, Docs. 92 and 162).

¹⁵¹ Eucken (1920a).

6.5 Adolf Kratzer and vibration-rotation spectra

In October 1920, Adolf Kratzer, a student of and, from 1918, an assistant to Sommerfeld, published a far more detailed and influential paper on the rotation-vibration bands of HCl.¹⁵² Kratzer began by pointing out a difficulty in an earlier work by Torsten Heurlinger: although Heurlinger’s use of a harmonic potential energy correctly led to a frequency shift proportional to the square of the rotational quantum number (see Eq. 30), it gave the wrong sign when compared with von Bahr’s and Imes’s experiments. Kratzer proposed to show that an anharmonic oscillator would show the correct behavior. Following Heurlinger, Kratzer used Bohr’s frequency condition throughout, remarking in a note that Kemble’s 1920 paper had done so only “in part.”¹⁵³

Kratzer’s thoroughgoing treatment introduced results and a notation that are still seen in modern textbooks. He derived an anharmonic correction term for zero rotation that, like Kemble’s, accounted for the harmonics not being integral multiples of the fundamental. Sommerfeld, in language similar to (if often a good bit clearer than) many modern textbooks, described Kratzer’s version of Eq. (30) as an interaction between vibration and rotation, in which the stretching of the molecule leads to both a larger moment of inertia and a smaller vibrational frequency.¹⁵⁴

Kratzer also had to explain the absence of a gap in Eq. (32). His solution was dramatically different from Reiche’s, whose 1920 paper he did not cite. He noted that Reiche’s theory of specific heats might seem to imply that any transition involving the rotation-free state ($m = 0$) could not appear; thus, both the $0 \rightarrow 1$ and $1 \rightarrow 0$ lines should be missing, as Reiche had assumed. But the width of the gap in Imes’s data, Kratzer pointed out, implied that only one of these lines is missing. He therefore assumed that the $m = 0$ state is not absent, but only unstable. Thus, a transition in which the molecule absorbs one rotational quantum as it goes from the $m = 0$ to the $m = 1$ rotational state is forbidden. But the one in which the molecule falls from $m = 1$ to $m = 0$ does appear! As Kratzer put it:

In order to understand this fact, we may assume that the rotation-free state is by no means impossible. The theory of specific heats and the absence of the zero line reveal merely that the probability for the existence of the rotation-free state is vanishingly small. This improbable state can rather be produced through external influences, but then exists only for a very short time....¹⁵⁵

This suggestion may seem improbable; and after the reappearance of half-quantum numbers in molecular spectra, it was roundly criticized. Walter Colby, for example,

¹⁵² Kratzer (1920). Comparatively little has been written about Kratzer. See Cassidy (2007), and Mehra and Rechenberg (1982–2000, Vol. 6, index), for references to minimal biographical information. See also the Wikipedia article, “Adolf Kratzer,” which seems to be drawn in considerable part from Mehra and Rechenberg.

¹⁵³ Kratzer (1920, p. 19).

¹⁵⁴ Sommerfeld (1922, Chapter VII, Sect. 2). My discussion is brief and incomplete. For more thorough accounts, see Brand (1995, esp. Chapter 9), Fujisaki (1983b, pp. 76–79), and Herzberg (1973). See also Ruark and Urey (1930, esp. pp. 376–380), where the treatment is almost identical to Kratzer’s; and Herzberg (1950, pp. 106–114), where it is nearly so.

¹⁵⁵ Kratzer (1920, p. 292).

observed several years later that although the $0 \rightarrow 1$ transition was absent, the “reverse transition, 1 to 0 absorption, is present—a fact very difficult to reconcile with the possibility of thermal equilibrium. This was an annoying difficulty for some time....”¹⁵⁶

Meanwhile, however, Kratzer’s suggestion was widely adopted. Eucken, who had been so puzzled by Imes’s data early in 1920, adopted Kratzer’s picture later that year, albeit at second hand.¹⁵⁷ Reiche himself adopted it in his 1921 textbook, as did Sommerfeld, who in the third edition of his *Atombau* remarked that the “deduction is surprising at first sight, and excellently confirmed by the behavior of the specific heat of rotation ... of hydrogen.”¹⁵⁸ Reiche’s and Einstein’s suggestion had vanished almost without a trace.¹⁵⁹

Nevertheless, half-quanta could not be denied. Kratzer himself introduced them in March, 1922 to explain the fine structure of the “cyan bands”—electronic transitions in the visible and ultraviolet region of the spectrum.¹⁶⁰ He attributed the half-quanta to an electronic orbital angular momentum directed perpendicular to the line joining the two nuclei (and thus parallel to the angular momentum of nuclear rotation about the center of mass). In a review article published later in 1922, Kratzer applied his new half-quanta only to the cyan bands, treating the infrared HCl spectra exactly as he had done in 1920.¹⁶¹ But in December 1922, in a long article devoted primarily to combined electronic, vibrational, and rotational transitions, he noted briefly that he had changed his mind, and now believed that *a priori*, both the $0 \rightarrow 1$ and the $1 \rightarrow 0$ transitions should be missing in the HCl fine structure, much as Reiche had concluded in 1920. Half-quanta, Kratzer said, entirely removed this difficulty, and even cleared up an inconsistency in his calculation of a numerical parameter in 1920.¹⁶²

Conversations between Kratzer and Werner Heisenberg almost certainly played a part in this story. The two had met in Sommerfeld’s Munich institute in 1921, at about the time that Heisenberg had begun to employ half-quanta himself in his “core model.”¹⁶³ Heisenberg later recalled that he and Kratzer had talked about half-quanta

¹⁵⁶ Colby (1926, p. 55). See footnote 167 below for a similar criticism by Hendrik Kramers and Wolfgang Pauli.

¹⁵⁷ Eucken (1920b, p. 380). Eucken did not cite Kratzer (1920), which had probably not yet appeared. Instead, he said this solution had been kindly called to his notice by Wilhelm Lenz, who had worked with Kratzer when both were studying under Sommerfeld. Eucken cited Reiche (1920), but only in support of Eq. (32); he apparently overlooked the postscript at the end, in which Reiche presented his and Einstein’s half-integral proposal.

¹⁵⁸ Sommerfeld (1922, Chapter 7, Sect. 2).

¹⁵⁹ I have come across only two passing references to Reiche’s and Einstein’s proposal during the years 1920–1926 when half-quanta were in vogue; see Sommerfeld (1924, footnote on p. 713), and Barker (1923) (from Randall’s Michigan group). Brand (1995, p.176) gives the only reference I have seen in the historical literature; and (in what may be a typographical error) he gets the date wrong.

¹⁶⁰ Kratzer (1922a). The “cyan bands” are a widely studied system of bands in the violet, associated with the radical CN (cyanogen); in the 1920s and earlier, they were sometimes associated with molecular nitrogen instead; see for example Sommerfeld (1922, Chapter 7, Sect. 3; 1924, Chapter 9, Sect. 3).

¹⁶¹ Kratzer (1922b).

¹⁶² Kratzer (1923a, p. 85). This paper was an “extension” of Kratzer’s Munich *Habilitation* thesis.

¹⁶³ For Heisenberg and half-quanta, see Cassidy (1992, esp. Chapters 7–8), and Cassidy (1979). Heisenberg’s first paper was dated December 1921, only a few months before Kratzer’s first use of half-quanta in March 1922, but well after Reiche (1920).

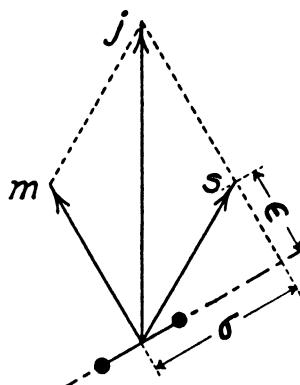


Fig. 6 Model of Kramers and Pauli (1923), taken from Kemble et al. (1926, p. 312). Here m is the rotational angular momentum associated with rotation of nuclei about the center of mass, perpendicular to the line joining the nuclei. The electronic orbital angular momentum s is rigidly oriented at a fixed angle to the line joining the two nuclei. Note the components ϵ and σ , respectively, parallel and perpendicular to the direction of m . Finally, j is the total angular momentum, quantized in integral units. To allow half-integral values of the rotational quantum number m in the hydrogen halides, Kramers and Pauli set $\sigma = 0$ and $s = 1/2$. For this case, j , m , and s are mutually parallel and in the direction of m in the Fig.

at length.¹⁶⁴ It must have been encouraging for these young physicists to see this strange and controversial notion emerging from such drastically different contexts.

6.6 Kramers, Pauli, and vibration-rotation spectra

At about the same time, early in 1923, Hendrik Kramers and Wolfgang Pauli elaborated on Kratzer’s introduction of an electronic angular momentum. In their model, the orbital electronic angular momentum was rigidly attached to the molecule at an arbitrary angle to the line joining the nuclei, and thus had components perpendicular and parallel to this line (Fig. 6). Max Born described it as a “top with an enclosed flywheel.”¹⁶⁵ Both the total angular momentum and the electronic angular momentum were quantized, the latter sometimes in half-quanta; as a result, the nuclear angular momentum was not quantized, but instead determined by geometry—the vector nuclear and electronic angular momenta had to add up to the integrally quantized total angular momentum. Molecular spectroscopists used this scheme for the next several years for spectra whose description required three rotational degrees of freedom. It served much the same function as the spin-orbit coupling schemes that Friedrich Hund would introduce in 1926, and that remain a staple of molecular spectroscopy textbooks.¹⁶⁶

¹⁶⁴ Thomas S. Kuhn, interview with Werner Heisenberg, AHQP, session 2 (7 February 1963), p. 13; session 3 (11 February 1963), pp. 18–19.

¹⁶⁵ Kramers (1923), Kramers and Pauli (1923), Born (1925, Sect. 19).

¹⁶⁶ Birge (1926), Hund (1926a). Kramers and Pauli rejected several possible configurations as mechanically unstable. Spectroscopists found them useful and employed them anyway. As Kemble remarked in

Kramers and Pauli devoted a long section in their joint paper to the infrared spectrum of HCl, and after rejecting two other possible approaches, independently adopted the same one that Kratzer had proposed: a half-integral angular momentum directed at right angles to the line joining the nuclei. Kramers and Pauli also pointed out the physical implication: “no rotation-free stationary state of the molecule exists.”¹⁶⁷

Later in 1923, Walter Colby at the University of Michigan further strengthened the case for half-quanta. Since 1921, Colby and his associates had been improving Imes’s measurements of the spectrum of HCl. In 1922, using a longer absorption chamber and an improved grating, they saw a “new group of faint lines...[that] appear only when the gas is heated (500° C), and ... may correspond to a change of radial [that is, vibrational] quantum from 1 to 2 although the frequencies do not agree with those predicted by Kratzer.”¹⁶⁸ A few months later, Colby, citing both Kratzer (1923a) and Kramers and Pauli, reported that he had recalculated the predicted frequencies using half-quanta and obtained good agreement.¹⁶⁹

Sommerfeld took note of these developments and adopted the new picture in the fourth (1924) edition of his *Atombau*. And in 1925, Marianus Czerny, another of the Berlin spectroscopists who had studied with Heinrich Rubens, clinched the case when in a difficult and innovative experiment he measured for the first time the pure rotational spectrum of HCl in the far infrared, and found a set of nearly evenly spaced rotational peaks that required half-quanta for their description.¹⁷⁰ Thus by the mid-1920s, the “old quantum theory,” supplemented by the mysterious and controversial but increasingly necessary half-quanta, had given a fully adequate description of the rotational and rotation-vibration spectra of HCl.¹⁷¹ In particular, Bohr’s frequency condition, an anharmonic potential, and the interaction between vibration and rotation accounted for the nonintegral harmonics and the spacings of the peaks. Half-quanta accounted for the gap in the center of the spectrum, for the transition between the $n = 1$ and $n = 2$ vibrational states, and even for the pure rotational spectrum in the far infrared. It was a remarkable achievement.¹⁷²

Footnote 166 continued

Kemble et al. (1926, p. 314), “In view of the uncertainty regarding the importance of dynamical stability for quantized motions this objection seems not to be crucial.”

¹⁶⁷ Kramers and Pauli (1923, p. 360). Kramers and Pauli knew that Kratzer had introduced half-quanta in electronic band spectra, but did not know that he had also adopted them for the infrared spectrum of HCl. They criticized his first attempt (Kratzer 1920) to explain the missing line, or gap, in the spectrum, commenting that it is “rather unsatisfactory,” before outlining their own explanation. Kratzer (1923a) had arrived at the *Annalen der Physik* in December 1922. Kramers and Pauli (1923) had arrived at the *Zeitschrift für Physik* only a month later; it is not surprising that they did not know of Kratzer’s change of heart.

¹⁶⁸ Colby and Meyer (1921), Colby et al. (1923, p. 7), Assmus (1992b, p. 14).

¹⁶⁹ Colby (1923); see also Colby (1926, pp. 54–57).

¹⁷⁰ Czerny (1925, 1927). For more on Czerny, see Helmut Müser, “Marianus Czerny,” <http://www.physik.uni-frankfurt.de/paf/paf144.html>.

¹⁷¹ To be sure, the introduction of half-quanta did lead to difficulties in calculating intensities. See Cassidy (2007), and Assmus (1992b).

¹⁷² In 1926, Kemble, in Kemble et al. (1926, pp. 16–17), said that only the wish to unify atomic and molecular models had required the rejection of Bjerrum’s picture, in which spectral lines directly represented mechanical frequencies. In her otherwise admirable and path-breaking analysis, Assmus (1992b, pp. 10–11) seems to agree, and even suggests that similar arguments apply to half-quanta (see esp. pp. 12–14).

7 Half-quanta and the specific heat of hydrogen

Almost immediately, theorists applied half-quanta to the specific heat of hydrogen: if half-quanta succeeded in describing one rotating dumbbell, might they not also work for the other? Alas, they did not. The American physical chemist Richard Chace Tolman made the first attempt.¹⁷³ He noted that “half quantum numbers have recently shown a surprising tendency to appear,” and cited a 1922 article by Kratzer in support. Tolman showed—the fourth time the idea had appeared independently—how half-quanta could account for the gap in the center of the hydrogen halide spectra.¹⁷⁴ With this encouragement, he went on to apply them to the specific heat of hydrogen. He counted degenerate states much as Reiche had done, and showed that the partition function was given by $Q = \sum_1^{\infty} 2ne^{-(n-\frac{1}{2})^2\sigma}$, where n is an integer, and where the rotator energies are given in the exponent. He calculated the specific heat in the usual way. His curve runs too high at 200 K, and much too low at room temperatures. Nevertheless, Tolman was encouraged. With considerable satisfaction, he pointed out that:

[It] should be noted how simply we have arrived at the conclusion that the a priori probabilities of the successive energy levels stand in the ratio 1, 2, 3, etc., without resorting to any artificial rejection of the states of no rotation....¹⁷⁵

He also suggested, citing Kemble and Van Vleck’s 1923 article, that vibrational contributions might raise the specific-heat curve at high temperatures, though he made no attempt to explore this possibility. He was particularly encouraged by his value for the moment of inertia, which was smaller than Reiche’s and closer to a result from hydrogen band spectra cited by Sommerfeld.

Erwin Schrödinger had long cast a skeptical eye on the specific heat of hydrogen. In a 1917 review article in *Die Naturwissenschaften*, he had contented himself with a graph that showed only a smooth line running through the data points. He all but ignored the theories, observing only that the approaches of Nernst, Einstein and Stern, Ehrenfest, and Planck “all lead to a more or less good explanation” of the data. He discussed none of these theories, observing only that, “We will not go into these

Footnote 172 continued

and 28). I think my analysis here shows just how central Bohr’s frequency condition and the introduction of half-quanta were. In 1926, for example, Van Vleck (1926a, p. 230) stated emphatically that, although half-quantum numbers are “in many respects decidedly illogical,” their use is “made plausible by the successful use of half-integers in interpreting frequencies in infra-red absorption bands.” Kemble himself had immediately qualified his statement, and had said even more forcefully in a letter to Raymond Birge a year earlier that Bjerrum’s theory was “early and erroneous” (Kemble to Birge, 25 February 1925, AHQP microfilm reel 50).

¹⁷³ Tolman (1923). See also the summary in Tolman (1927, Chapter 9). In 1927, Tolman worked primarily with the old quantum theory, though after summarizing his 1923 paper, he observed that “The final acceptable treatment of the quantum states of the dipole rotator and their a-priori probabilities will perhaps have to be based on the new dynamics” (p. 108).

¹⁷⁴ Tolman (1923) cited only Kratzer (1922b), in which Kratzer (as already noted) introduced half-quanta for visible bands (electronic transitions), but retained his 1920 explanation for the gap in the HCl spectrum. Moreover, Tolman’s analysis leading to half-quanta was notably different from either Kratzer’s or Reiche’s.

¹⁷⁵ Tolman (1923, p. 474).

circumstances more closely, since they are still by no means resolved.” He did point out, much as Nernst had done in 1911, that quantum theory had cleared up earlier problems with the specific heats of gases.¹⁷⁶

Schrödinger was no less skeptical in 1924, when in an article in the *Zeitschrift für Physik*, and at more length in a review of specific heats in the *Handbuch der Physik*, he himself turned to the specific heat of hydrogen.¹⁷⁷ Like Tolman, he adopted half-integral quantum numbers, noting that the “approach first introduced into band spectra by Kratzer not only made the absence of rotation-free states understandable without special assumptions,” but also explained the gap in the middle of the band. However, instead of finding the weights in the partition function by counting degenerate states or by calculating the size of phase-space cells, he simply noted that, “The claims of theory are on this point … so uncertain, that one might do better to fit the weight ratios as well as possible to the observations.”¹⁷⁸ In this spirit, he wrote the partition function as $\sum g e^{-\varepsilon/kT}$, and gave two possible sets of weights,

$$g_1 : g_2 : g_3 = 1 : 2 : 4 \text{ (curve A) and } g_1 : g_2 : g_3 = 4 : 7 : 17 \text{ (curve B),}$$

chosen to match the data as closely as possible without exceeding the equipartition value at high temperatures. The results were reasonably good, and Curve B in particular was an improvement over Reiche’s Curve V. Nevertheless, both overshot the “fatal point” (as Schrödinger called it) at 200 K, and came in slightly low at room temperature. There, at least, he could call attention to new room temperature measurements, “to which Herr Eucken kindly directed me,” that promised better agreement.

Like Tolman, Schrödinger appealed to the band spectra of hydrogen to justify half-quanta. He first noted that, “Without doubt, better agreement with the simple dumbbell model [whole quanta] would be achieved if one liberalized the choice of weights”.¹⁷⁹ As he pointed out, however, the moments of inertia from his theory agreed more closely with those drawn from hydrogen band spectra as well as from measurements of the “entropy constant”—the constant in what is today usually called the Sackur–Tetrode equation for the entropy of an ideal gas.

Thus, over a decade after Einstein and Stern had first taken up the problem, physicists had still not found a quantitatively accurate theory for the specific heat of hydrogen. Even the introduction of the half-quanta, which had worked so well for molecular spectra, had not led to a more accurate theory, though they at least made the prohibition of rotation-free states seem less arbitrary. Schrödinger’s resort to arbitrary weights, in an attempt, however empirical, to find a better fit to the experimental data, shows just how seriously he and his contemporaries took the failure to find a satisfactory theory for the specific heat of hydrogen.

¹⁷⁶ Schrödinger (1917, p. 566); see also Schrödinger (1919).

¹⁷⁷ Schrödinger (1924, 1925).

¹⁷⁸ Schrödinger (1925, p. 296), Schrödinger (1924, p. 344).

¹⁷⁹ Schrödinger (1924, p. 346).

8 New data and a new quantum mechanics

The year 1924 brought the first of several new measurements of the specific heat of hydrogen,¹⁸⁰ the first to appear since those of Scheel and Heuse in 1913. These experiments often employed new and innovative experimental techniques, and by 1925 led to occasional bickering among some experimentalists, eager to explain small discrepancies by criticizing their competitors’ techniques and data reduction.

In band spectra, 1924 also saw the discovery of a surprising new effect: rotational lines of alternating intensity in the electronic band spectra of diatomic molecules with identical nuclei. This phenomenon, first seen by the German spectroscopist Reinhard Mecke in singly ionized nitrogen,¹⁸¹ was followed by the discovery that in molecular helium and oxygen, every other rotational line was absent. One attempted explanation by Gerhard Dieke, at the time a student of Ehrenfest in Leiden, involved quarter-quanta, a suggestion that was roundly denounced by such figures as Heisenberg and Van Vleck.¹⁸² Dieke also attempted a treatment of the specific heat of hydrogen using quarter-quanta, with only limited success.¹⁸³ However, the connection Dieke saw between the specific heat of hydrogen and the lines of alternating intensity figures prominently in the final stages of our story.

The following years also saw the birth of modern quantum mechanics. Heisenberg’s 1925 “reinterpretation” paper led to the matrix mechanics of Born, Heisenberg, and Jordan. Schrödinger’s papers on wave mechanics followed in 1926. Just as in the old quantum theory, the rotator was a central problem, straightforward to solve and essential to molecular physics. Heisenberg and Schrödinger both gave solutions for the rigid rotator.¹⁸⁴ Others, including Reiche, David Dennison, and Isidor I. Rabi and Ralph de Laer Kronig, employed both matrix and wave mechanics to give more general solutions that included the symmetric as well as the rigid rotator. These results led to new theories of molecular spectra that were nearly identical to the generally successful efforts of the old quantum theory.¹⁸⁵

One prominent result was the justification of the mysterious half-quanta. As both Heisenberg and Schrödinger pointed out, the energy of a rigid rotator using half-quanta

¹⁸⁰ Trautz and Hebbel (1924), Brinkworth (1925), Giacomini (1925), Partington and Howe (1925), and Cornish and Eastman (1928); see Figs. 8 and 11. Giacomini’s data had been taken in Nernst’s Berlin laboratory in 1922, but were not published until 1925. His data and Brinkworth’s covered the region around 200 K and showed a slightly higher specific heat than Eucken (1912) and Scheel and Heuse (1913) had measured. Cornish and Eastman’s more comprehensive measurements in 1928 confirmed this result.

¹⁸¹ Mecke (1924).

¹⁸² See Birge (1926, pp. 200–214) for discussion and bibliography. Kratzer (1923b) had raised the possibility of quarter-quanta a year earlier in a different context.

¹⁸³ Dieke (1925). See also the letter of Dieke to Van Vleck, 9 October 1925, AHQP microfilm reel 49, in which Dieke stated that Einstein had encouraged his efforts. He also said that he was not satisfied with his results, but that Ehrenfest had encouraged him to publish. Perhaps for that reason, his paper appeared in *Physica*, at that time a journal published in Dutch.

¹⁸⁴ Heisenberg (1925, p. 274), Schrödinger (1926a, p. 35), Schrödinger (1926b, p. 1061).

¹⁸⁵ Reiche (1926), Rademacher and Reiche (1926), Dennison (1926), Kronig and Rabi (1927); see also Ruark and Urey (1930, Chapters 12, 19), Cassidy (2007).

is equal to the new quantum-mechanical result within a numerical constant. Thus, if m is an integer, then the energy E of a rigid rotator is

$$E = \left\{ \left(m + \frac{1}{2} \right)^2 - \frac{1}{4} \right\} \frac{\hbar^2}{8\pi^2 J} = m(m+1) \frac{\hbar^2}{8\pi^2 J}. \quad (35)$$

The term on the right-hand side is of course the modern value.

John H. Van Vleck was among the first to apply the new quantum mechanics to the specific heat of hydrogen. In August 1926, he and his first Ph.D. student at the University of Minnesota, Elmer Hutchisson, published an impressive two-part review article in *The Physical Review*. This work had begun in 1924 as an attempt to extend Tolman's half-quanta model to high temperatures, but was quickly adapted to the new theory.¹⁸⁶ Van Vleck gave an extensive theoretical discussion, while Hutchisson compared the various specific-heat theories with experiment. Van Vleck began by noting that "the quantum theory has been revolutionized by the new mechanics...." Much as Reiche had done in 1919, he systematically and thoroughly worked through the various possibilities—among them Reiche's "whole quanta," even though "it is very doubtful that they are allowable in the new quantum mechanics"; the "half quanta" of the new mechanics (he consistently preferred the language of the old quantum theory); different weights; and both rigid and elastic rotators.¹⁸⁷

As in 1923, Van Vleck was interested in the behavior of the specific heat far above room temperatures, at which vibrational degrees of freedom are excited. His most successful model used the elastic rotator that he and Kemble had developed in 1923. As he showed, their complex expression for energy was unchanged in the new quantum mechanics apart from the use of half-quanta. The weights were those of the new quantum mechanics; and like everyone since Ehrenfest, they used the energies and weights to calculate the partition function and the specific heat. The result was discouraging: "Unfortunately, an impossible specific heat curve is obtained ... from the simple theory of the rotator in the new mechanics...."¹⁸⁸ That curve, he explained, was similar to Planck's, reaching a high, broad peak before eventually dropping to the equipartition value. With considerable insight, he said that:

The failure of the simple theory is doubtless due to the non-polar character of the hydrogen molecule and is probably intimately connected with the alternating intensities found in the band spectra of certain non-polar molecules.¹⁸⁹

Significantly, Van Vleck fastened on the "non-polar character" of the hydrogen molecule, rather than its two identical nuclei. But he did not see how to apply this insight, even though, as he reported, Bohr, Kramers, Born, and Heisenberg had all suggested to him (correctly, it turned out) that:

¹⁸⁶ See the letters of Van Vleck to Kemble, 1 December 1924, AHQP microfilm reel 49 and Kemble to Birge, 13 April 1925, reel 50. See also two abstracts for 1924 APS meetings, Van Vleck (1924), and Hutchisson and Van Vleck (1924).

¹⁸⁷ Van Vleck (1926b), Hutchisson (1926). The quotations are on p. 980 and p. 985 of Van Vleck's paper.

¹⁸⁸ Van Vleck (1926b, p. 985).

¹⁸⁹ Van Vleck (1926b, p. 980).

[It] appears likely that the alternating intensities are in some way connected with the extension of the Pauli exclusion principle which has recently been developed by Heisenberg in applying the new quantum mechanics to the spectrum of neutral helium....¹⁹⁰

Van Vleck was no novice in quantum theory, as both his insightful textbook and his own research clearly show. Other publications show how quickly he had absorbed the new theory.¹⁹¹ This episode serves to remind us of the strange and unexpected behavior of indistinguishable particles in quantum mechanics, and shows how difficult it was even for someone as exceptional as Van Vleck to see the implications of these new ideas.

Van Vleck was therefore reduced to the same sort of arbitrary artifices that Reiche had employed:

We shall list below several specific ways of crawling out of the specific heat dilemma by assuming more or less empirically a different quantization than in the simple polar rotator. Most of the suggestions appear rather artificial and are frankly only conjectures.¹⁹²

Van Vleck’s most successful attempt, like Reiche’s, arbitrarily excluded the first term in his partition function, corresponding to the lowest rotational energy state. He pronounced the resulting curve “in quite satisfactory agreement with the observed data.”¹⁹³

Hutchisson, whose paper compared the various theories with the data, was more restrained. Even with new data that showed somewhat higher specific heats around 200 K, Hutchisson pointed out “a real discrepancy between experiment and theory in the slope of the specific heat curves between 120° and 220° K.” He added that “it is necessary to consider not only the rotational energy ... but also the vibrational energy and the increase of energy which is caused by the expansion of the molecules due to centrifugal forces.”¹⁹⁴ This step involved treating the (unknown) vibrational frequency in the ground state as a free parameter. Without it, Van Vleck’s curve would have come in too low at room temperature. Van Vleck seems to have been of two minds about this curve; on the one hand, he said, along the lines of the passage quoted above, that: “It is hard to imagine any theoretical basis for the complete exclusion of the [lowest energy] state....”¹⁹⁵ On the other hand,

one must at the same time realize that observed specific heats furnish fairly definite evidence as to what a priori probabilities [weights] and ranges of quantum

¹⁹⁰ Van Vleck (1926b, p. 1003).

¹⁹¹ Van Vleck (1926a) (textbook); and, for example, Van Vleck (1926c). See also Duncan and Janssen (2007) for Van Vleck’s work on dispersion theory.

¹⁹² Van Vleck (1926b, p. 986).

¹⁹³ Van Vleck (1926b, p. 987).

¹⁹⁴ Hutchisson (1926, pp. 1023 and 1024–1025).

¹⁹⁵ Van Vleck (1926b, p. 988).

numbers are legitimate. For this reason, it does not appear altogether unlikely that the true specific heat curve is of the form ... given below.¹⁹⁶

In short, Van Vleck had found a curve that, if not perfect, gave reasonable agreement with the data. The fit was noticeably better than Reiche's curve V—but like Reiche's, it came at the cost of an arbitrary and entirely mysterious assumption.¹⁹⁷

Van Vleck did not stop there. He went on to consider, and reject, models based on the symmetric (or gyroscopic) rotator, on the grounds that an electronic angular momentum would result in a paramagnetic molecule.¹⁹⁸ Experimentally, however, hydrogen was diamagnetic. He refuted a suggestion made to him by Hendrik Kramers that Bose–Einstein statistics might somehow come into play. He devoted a long section to band spectra, and considered at length, in the context of both the specific heat and the band lines of alternating intensity, a theory of Ehrenfest and Tolman that argued for the exclusion of every other state in nonpolar molecules, and a related proposal by his friend John C. Slater.¹⁹⁹ He considered and rejected Dieke's “unreasonable ‘quarter quanta’.”

Van Vleck concluded with a section on the chemical (or entropy) constant. He pointed out that, in principle, this constant should shed light on both *a priori* probabilities and moments of inertia. Alas, the remainder of his discussion pointed out the inadequacies in both theory and experiment. He glumly concluded that “the correlation of experimental and theoretical chemical constants is at present in a decidedly chaotic state.”²⁰⁰ Van Vleck later expressed considerable dissatisfaction with this paper.²⁰¹ It was nevertheless a thorough and insightful survey of the state of theory and experiment towards the end of 1926. Even the advent of the new quantum mechanics did not at first point the way towards a solution of this long-standing dilemma.

Despite these unpromising beginnings, a successful description of the specific heat of hydrogen emerged in the new quantum mechanics less than a year later. It is convenient to identify four stages:

- In June 1926, Werner Heisenberg discovered the unexpected behavior of identical particles in quantum mechanics and used this discovery to analyze the spectrum of helium (Sect. 9).

¹⁹⁶ Van Vleck (1926b, p. 986).

¹⁹⁷ Hutchisson's curve fell much closer to the new data at 200 K than did Reiche's Curve V. It is, however, difficult to determine exactly how Hutchisson did the calculations, which must have been horrendously complex. I cannot reproduce his results exactly from the equations and parameter values that he listed. His Ph.D. thesis consists of reprints of two publications, including this one, and so provides no additional insight into his calculations. It later turned out that vibrational degrees of freedom are not excited until well above room temperature and that the effect of centrifugal expansion on the specific heat is negligible.

¹⁹⁸ A promising gyroscopic model based on the old quantum theory, cited by both Van Vleck (1926b) and Hutchission (1926), had been developed by Hans Lessheim (1926), a student of Reiche's at Breslau. Both Lessheim and Reiche (1926, p. 455) rejected this model on a quite different basis: it implied a moment of inertia, 3×10^{-41} gm cm², that they thought was larger than was allowed from molecular spectra measurements (see Table 1). Ironically, this value turned out to be considerably too small.

¹⁹⁹ Ehrenfest and Tolman (1924), Slater (1926).

²⁰⁰ Van Vleck (1926b, p. 1021). See also Desalvo (1992), Darrigol (1991, esp. pp. 270–278).

²⁰¹ Van Vleck to Dennison, 23 October 1967, in the Dennison Archive, Box 1, Bentley Library, University of Michigan. See also Fellows (1985, Chapter 2, esp. p. 39).

- In December 1926 and February 1927, Heisenberg and Friedrich Hund applied these ideas to molecular spectra, and Hund tried to extend them to the specific heat of hydrogen (Sects. 9, 10).
- In 1926 and 1927, a breakthrough in experimental spectroscopy led to the first accurate spectroscopic measurement of the moment inertia of molecular hydrogen (Sect. 11).
- In May 1927, the American theorist David Dennison took advantage of all of these developments to construct the modern quantum-mechanical theory of the specific heat of hydrogen (Sect. 12).

9 Werner Heisenberg, indistinguishable particles, and the spectrum of helium

The spectrum of helium presented another unsolved problem in the old quantum theory.²⁰² Energy levels, particularly that of the ground state, had proven impossible to calculate accurately. Moreover, the spectrum of helium (similar to that of the alkaline earths) was divided into two noncombining term series, named parahelium and orthohelium. The first consisted of singlets; the second were thought to consist of doublets until 1926, when their triplet structure was predicted by Heisenberg and confirmed by experiment.²⁰³

Matrix mechanics did not originally encompass many-body problems. Thus it was a considerable triumph for the new theory when Heisenberg, in a series of three papers in late 1926 and early 1927, uncovered the surprising behavior of identical particles in the new quantum mechanics, explained the noncombining para and ortho term series in helium, and made a start at the calculation of energy levels.²⁰⁴ Heisenberg recalled, years later, that “this paper was also full of excitement for me because so many new things came up.”²⁰⁵

Heisenberg began his first paper by criticizing Schrödinger’s conceptual picture of wave mechanics, even as he was showing how useful its formalism could be—and indeed, he would find Schrödinger’s wave mechanics essential. Then, in what resembled an undergraduate classical-mechanics lecture, he reviewed the familiar textbook problem of two coupled harmonic oscillators,²⁰⁶ arguing that it was the “simplest conceivable many-body problem” and at the same time “possesses all characteristic properties of the quantum-mechanical … problem.” He wrote the standard Hamiltonian for two coupled harmonic oscillators,

²⁰² Small (1971), Darrigol (1992).

²⁰³ Houston (1927).

²⁰⁴ Heisenberg (1926a,b, 1927). For a contemporary account, see Birtwistle (1927, Chapters 26 and 27). See also Carson (1996). Dirac (1926) independently discovered the implications of quantum mechanics for identical particles at about the same time, and better understood the connection to gas statistics, but did not treat helium. Fermi (1926) likewise worked in the context of ideal gas theory. See Jammer (1966–1989, pp. 341–343), Desalvo (1992).

²⁰⁵ Heisenberg, AHQP interview (footnote 164), session 8 (27 February 1963), pp. 22–23.

²⁰⁶ In his AHQP interview (footnote 164), Heisenberg recalled that coupled oscillators had been much discussed in Göttingen and Copenhagen around this time, “especially in connection with dispersion.” See session 8 (27 February 1963), p. 25.

$$H = \frac{1}{2m}p_1^2 + \frac{m}{2}\omega^2q_1^2 + \frac{1}{2m}p_2^2 + \frac{m}{2}\omega^2q_2^2 + \lambda q_1q_2, \quad (36)$$

where the p s and q s are momentum and position coordinates and λ is a coupling constant. The normal modes are given by

$$q'_1 = \frac{1}{\sqrt{2}}(q_1 + q_2); \quad q'_2 = \frac{1}{\sqrt{2}}(q_1 - q_2), \quad (37)$$

for which, of course, the two masses oscillate either in phase or 180° out of phase, with different frequencies.

Heisenberg used Eq. (37) to write Eq. (36) in terms of the normal modes, and quantized the resulting Hamiltonian to obtain

$$H_{n'_1, n'_2} = \frac{\omega'_1 h}{2\pi} \left(n'_1 + \frac{1}{2} \right) + \frac{\omega'_2 h}{2\pi} \left(n'_2 + \frac{1}{2} \right), \quad (38)$$

thus describing two independent normal-mode oscillators with quantum numbers n'_1 and n'_2 . He then supposed the masses to be charged, and investigated both dipole and higher-order transitions between quantum states labeled by (n'_1, n'_2) , using an argument apparently drawn from the correspondence principle and not depending on the new quantum mechanics.

Figure 7 shows the remarkable result: the states separate into what Heisenberg called + and • states. Like states could combine with one another, but combinations between + and • states were absolutely forbidden. He noted a “characteristic uncertainty”: are both term systems present in nature, or only one? Heisenberg argued that this “characteristic resonance” (as he called it) between coupled systems could apply not only to harmonic oscillators in classical physics, but also to more general systems in quantum mechanics: “I would like to show that coupled systems in quantum mechanics always behave similarly to the above-explained example.”²⁰⁷

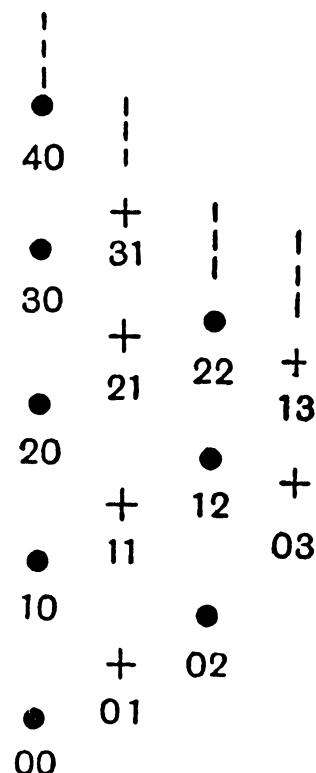
Heisenberg began with two identical unperturbed systems coupled by an interaction Hamiltonian that he treated as a perturbation. Since the two systems have identical energy levels, the combined system is degenerate; hence he used degenerate first-order perturbation theory in matrix mechanics to calculate the perturbed energy levels that lifted the degeneracies. Again he found noncombining + and • term systems whose energies were shifted by the perturbation. He then turned to Schrödinger’s wave mechanics, and found that the corresponding wave functions must be either even or odd under exchange.²⁰⁸

Heisenberg turned next to the problem of two identical electrons in a helium atom, for which the perturbation was the Coulomb interaction between the two electrons.

²⁰⁷ Heisenberg (1926a, p. 416).

²⁰⁸ Heisenberg’s physical picture, “resonance,” envisioned the two identical systems exchanging energy, in analogy to the normal modes of his coupled oscillators. In the case of the helium atom, he even raised tentatively the possibility of the two electrons constantly changing positions. See Carson (1996).

Fig. 7 Heisenberg’s (1926a) energy diagram for the coupled oscillators that he used to investigate the noncombining singlet and triplet states in helium, taken from Birtwistle (1928, p. 217). The numbers refer to the quantum numbers n'_1 , n'_2 , the quantum numbers for the even and odd normal modes (Eq. 38). Heisenberg showed that transitions between + and • states were absolutely forbidden



The • and + states corresponded to parahelium and orthohelium respectively; intercombinations were “for the time being” completely prohibited. He then introduced spin, and noted (in what has become a standard textbook result) that for the two-electron system, there should be one antisymmetric and three symmetric spin states—the latter thus had a greater statistical weight. The resulting spin-orbit interaction, as it is called today, relaxed the prohibition and permitted weak intercombinations between para- and orthohelium.

However, because spatial and spin states must combine to give the total symmetry of the system, Heisenberg was now faced with the prospect of *two* complete and independent para and ortho systems:

The one system describes a term spectrum for which orthohelium is a triplet system, parahelium a singlet, the other a term spectrum for which orthohelium is a singlet system and parahelium a triplet. Intercombinations between parahelium and orthohelium are allowed ... owing to the strength of the interaction between orbit and electron magnet. In contrast there are no intercombinations between the + and • systems.²⁰⁹

²⁰⁹ Heisenberg (1926a, p. 422)

Only one of these systems exists in nature; but which one? Heisenberg argued that the significance of Bose–Einstein counting was to reduce the $n!$ possibilities in classical theory to one; and the Pauli exclusion principle—the “ban of equivalent orbits” as Heisenberg called it—is “automatically satisfied” if the \bullet system (corresponding to an antisymmetric total wave function) is chosen. In this way, he argued, both Bose–Einstein counting and the Pauli principle found a natural home in quantum mechanics.

Heisenberg returned to this theme in his third paper of this series, dated December 1926. But now the identical particles were nuclei in diatomic molecules. And the physical problem was the recently discovered presence of lines of alternating intensity in the electronic spectra of such diatomic molecules. He observed that no satisfactory solution had emerged in the old quantum theory, referring at one point to the “notorious quarter-quanta” that Gerhard Dieke had brought to bear on both alternating intensities and the specific heat of hydrogen.²¹⁰

Heisenberg’s solution was to connect “the intensity alterations with a resonance in the nuclei.”²¹¹ By introducing nuclear spin, he could create para and ortho systems analogous to those he had found for helium. Here, however, the critical feature was the different weights associated with symmetric and antisymmetric nuclear spin states. Those different weights would result in different transition probabilities among para and ortho nuclear spin states, and hence to the experimentally observed alternating intensities observed in molecular band spectra.

Heisenberg proceeded much as he had done for helium. Using Schrödinger’s wave-function language freely, he noted that the total molecular eigenfunction was the product of eigenfunctions for center-of-mass motion, nuclear oscillation, electronic motion, and nuclear rotation—he added nuclear spin later. The first two are always symmetric in the nuclear coordinates. The rotational wave function is symmetric for even rotational quantum numbers, antisymmetric for odd. Finally, the electronic wave function is either symmetric or antisymmetric under the exchange of *nuclei*, a result he credited to a work in press by his friend and colleague Friedrich Hund. Both physicists were at Bohr’s Institute for Theoretical Physics in Copenhagen late in 1926 and early in 1927, and judging by their papers and later recollections, they were talking about this problem extensively.²¹²

Heisenberg first assumed that the two nuclei are “spherically symmetric” (that is, had no nuclear spin). Under these circumstances, for a given electronic state, either the odd or the even rotational states should be missing, since both the total and electronic wave functions must be either odd or even. And indeed, as he pointed out, spectroscopists had seen such missing lines in the spectra of molecular helium and oxygen.

Heisenberg then completed the analogy to helium by introducing nuclear spin. With this step, there were again two systems that could not combine, analogous to his earlier

²¹⁰ Heisenberg did not mention Dieke by name. See Van Vleck (1926b), and Birge (1926) for bibliography and discussion of Dieke’s papers.

²¹¹ Heisenberg (1927, p. 262).

²¹² See Heisenberg (1927, pp. 262, 264); Thomas S. Kuhn, interview with Friedrich Hund, AHQP, session 2 (25 June 1963), p. 10; session 3 (26 June 1963), p. 22; and also Heisenberg, AHQP interview (footnote 164), session 5 (15 February 1963), p. 12.

$+$ and \bullet states. As before, each one had weakly interacting para and ortho terms. He tentatively assumed spin-1/2 nuclei and a totally antisymmetric wave function (analogous to \bullet), “in order to make the analogy of the statistics of protons to electrons complete,” though he immediately added that “one cannot be certain which system is selected.” Given his choice, transitions between ortho terms (odd rotational quantum number in the ground state), weighted more heavily by the nuclear-spin triplets, should be brighter than transitions between para states. As we have seen, such alternating intensities had already been observed for N_2^+ , and, Heisenberg added, “perhaps also with H_2 .²¹³

10 Friedrich Hund and the specific heat of hydrogen

Friedrich Hund submitted his paper for publication in February 1927, only 2 months after Heisenberg’s.²¹⁴ Hund’s paper was the third in a series of groundbreaking papers on molecular spectra, in which he combined the new quantum mechanics with a series of vector models for angular momentum and the beginnings of what became known as molecular orbital theory. Hund also investigated the symmetries that characterize diatomic molecules with both identical and dissimilar nuclei.²¹⁵ His contributions in these papers remain staples of the textbook literature. It is thus ironic that, like so many others, he came to grief over the specific heat of hydrogen.

After treating the properties of the electronic states of diatomic molecules with identical nuclei, Hund turned to the lines of alternating intensity that Heisenberg had previously discussed. Hund adopted an almost identical theoretical picture, noting for example that: “*The intensity alterations signify that systems symmetric and also antisymmetric in the nuclei both appear, but with different statistical weights*” [Hund’s emphasis].²¹⁶ Hund noted that by assuming “a new property of the nucleus” (unlike Heisenberg, he never spoke explicitly of nuclear spin), a particular total wave-function symmetry could be chosen. (In other words, the total wave function for the molecule, $\Psi_{\text{total}} = \psi_{\text{electronic}} \psi_{\text{rotational}} \psi_{\text{nuclear}}$, could be either odd or even *under the exchange of nuclei*.) Hund had already shown that for the ground state, $\psi_{\text{electronic}}$ was even. Thus, just as Heisenberg had argued, odd and even rotational states were associated with odd and even nuclear wave functions, resulting in weakly combining para and ortho states whose different statistical weights, stemming from the different weights of the nuclear wave function, could explain the alternating intensities. But these different weights also had implications for the specific heat of hydrogen.

²¹³ Heisenberg (1927, pp. 264–265).

²¹⁴ Hund (1927).

²¹⁵ My brief summary here does not do justice to an exceedingly complex topic. The historical literature describing both the experimental and theoretical description of molecular spectra as it had developed in the mid-1920s, including Hund’s work, is comparatively sparse. But see Gavroglu and Simões (1994), Kutzelnigg (1996), Cassidy (2007), Mehra and Rechenberg (1982–2000, Vol. 6, Chapter 3), and Brand (1995, Chapters 11 and 12). For contemporary accounts, see Kemble et al. (1926), and Ruark and Urey (1930, esp. Chapter 12).

²¹⁶ Hund (1927, p. 113).

Hund observed that although the lines of alternating intensity in singly ionized nitrogen had been seen, a nitrogen nucleus must be "a rather intricate structure," and that the investigation of the simpler hydrogen nucleus might be revealing:

A determination of the properties of the hydrogen nucleus would be very interesting. An intensity alteration is perhaps present in the bands of the H₂ molecule; but it is not wholly certain. But we have yet another criterion, the behavior of the specific heat of hydrogen at low temperatures....

We will show in the following section that the empirical behavior of the specific heat of hydrogen can be explained if one assumes that the even rotation states of the ground term have an approximately doubled statistical weight....²¹⁷

Hund had thus shown, for the first time, how nuclear spin could affect the specific heat of hydrogen by forcing different weights for odd and even rotational states in the partition function. But his assumption that the weights of the even rotational states were double those of the odd ones led him to conclude, in sharp contrast to Heisenberg's tentative assumption, that the total wave function for the hydrogen molecule must be symmetric:

Thus, if one wants to express the properties of hydrogen nuclei so that only one of the two symmetry systems appears, then one must assume a new property of the nucleus and further assume that only term systems *symmetric in the nuclei* [my emphasis] appear. It therefore shows a different behavior from two electrons.²¹⁸

This choice was entirely empirical. Hund's partition function took the form:

$$Q = \beta \left(\sum_{m \text{ even}} (2m+1)e^{-E_m/kT} \right) + \sum_{m \text{ odd}} (2m+1)e^{-E_m/kT}, \quad (39)$$

where β is the ratio of even-to-odd rotational states. He calculated the specific heat in the usual way. Note his implicit assumption: weak intercombinations between odd and even rotational states maintained thermal equilibrium as the temperature changed. In what must have been tedious arithmetic calculations, he plotted the specific heat for at least nine values of β ranging from zero to infinity, and found that:

[The] theoretical curve with $\beta = 2$ satisfactorily describes the empirical results. Naturally we can not infer exactly $\beta = 2$ from the curves; thus for example the departure is also not very large with $\beta = 3$.²¹⁹

As he did not point out but surely knew, these values of β are the appropriate choices for a symmetric total wave function and nuclear spin 1 and 1/2, respectively.²²⁰ This

²¹⁷ Hund (1927, p. 114).

²¹⁸ Hund (1927, p. 115).

²¹⁹ Hund (1927, p. 120).

²²⁰ In general, $\beta > 1$ implies symmetric total wave functions, $\beta < 1$ anti-symmetric ones. Heisenberg, for example, had found that for two spin one-half particles, there would be one antisymmetric and three symmetric *spin* states. But for a totally antisymmetric wave function, symmetric (even) rotational states are combined with antisymmetric (odd) nuclear spin states, and vice versa; so in Heisenberg's version,

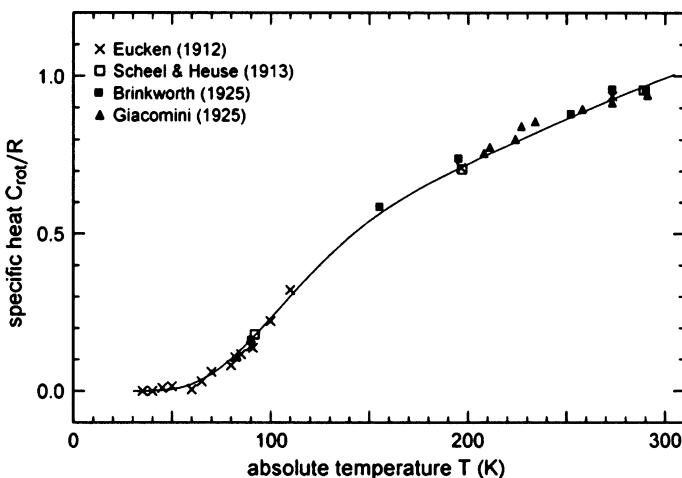


Fig. 8 Specific heat curve of Friedrich Hund (1927). Note that Hund’s curve is still rising at room temperature. If extended to higher temperatures, his curve reaches a peak at around 500 K, about 1.2 on the scale in this graph, before slowly returning to the equipartition value. As far as I know, no one noticed this behavior at the time

Table 1 Comparison of moments of inertia of hydrogen derived from specific heats and from molecular spectra

<i>J</i> from the specific heat of hydrogen		<i>J</i> from molecular spectra	
Source	<i>J</i> (in gm cm ²)	Source	<i>J</i> (in gm cm ²)
Reiche (1919)	2.2 to 2.3×10^{-41}	Lenz (1919)	1.85×10^{-41}
Schrödinger (1924)	1.43 to 1.48×10^{-41}	Allen (1924)	1.5 to 1.8×10^{-41}
Van Vleck (1926)	2.0 to 3.0×10^{-41}	Curtis (1925)	1.25 to 1.8×10^{-41}
Hund (1927)	1.54×10^{-41}		

close agreement with the data must have seemed encouraging (Fig. 8).²²¹ In addition, all of Hund’s plots for $\beta < 1$ showed a distinct peak, apparently confirming his choice of a symmetric total wave function. Finally, his value for the moment of inertia of the hydrogen molecule, 1.54×10^{-41} gm cm², was in good agreement with earlier results (see Table 1).

Footnote 220 continued

the 1:3 ratio of odd to even spin states implied a 1:3 ratio of even to odd *rotational* states, or $\beta = 1/3$ in Hund’s language. Hund, by contrast, linked even rotational states with even nuclear spin states, and odd with odd, to give a symmetric total wave function. Both Hund and Heisenberg understood these points; they did not yet know the connection between spin and statistics, and did not know which symmetry was obeyed by the hydrogen molecule.

²²¹ Note, however, that Hund’s curve (Fig. 8) has a large positive slope at room temperature. Had Hund plotted his theoretical curve at higher temperatures, he would have discovered that it continued to rise to a peak about 20% above the equipartition value around 450 K before converging to the equipartition value at still higher temperatures. As far as I know, no one noticed this behavior at the time. Hund’s curve was rejected for other reasons; see below.

Nevertheless, Hund knew of one potential cloud on the horizon. After his detailed discussion of alternating intensities and just before he presented his specific-heat calculations, we find the following enigmatic remark:

The term systems of the H_2 molecule given by Dieke and Hopfield, together with an analysis of the band structure that Hori has carried out with the bands of Werner and Witmer, have not yet been brought into agreement with the theoretical statements made here.²²²

11 Experimental molecular spectroscopy and the moment of inertia of hydrogen

To understand Hund's observation, we must turn to electronic transitions in molecular spectra and their relation to moments of inertia. The moment of inertia is a free parameter in models of the specific heat of hydrogen. We have seen how theorists, beginning with Einstein and Ehrenfest, chose values that brought theory and observations into agreement at the lowest temperatures. But molecular moments of inertia could also be measured directly, in the combined electronic, vibrational, and rotational transitions in molecular spectra of diatomic molecules. Such transitions are seen even in diatomic molecules like hydrogen, which do not show vibration-rotation spectra since they have no electric dipole moment.²²³ Such measurements thus offered a second and independent route to the moment of inertia of the hydrogen molecule. Both Tolman and Schrödinger compared their own estimates with ones drawn from molecular spectra.

Throughout the early and mid-1920s, as Table 1 shows, values drawn from specific heat models and molecular spectra were at least roughly consistent. That apparent agreement, however, did not last. To understand why, and to see how a new value emerged, we must understand in more detail the difficulties in interpreting the spectrum of molecular hydrogen.

The study of molecular band spectra, particularly in the visible and ultraviolet, predates quantum theory. By 1920, it was understood that "bands"—diffuse and apparently continuous structures with a sharp "head" at one end—corresponded to electronic transitions (Fig. 9a). It had also become widely accepted that energy differences between electronic states were larger than those separating vibrational states, and that those differences were in turn larger than those separating rotational states.²²⁴

A particular band represents a transition between different vibrational levels in different electronic states. Sophisticated measurements and techniques of data analysis allowed spectroscopists to identify "progressions" and "sequences" of bands corresponding to transitions between different vibrational levels of the same pair of electronic states. Moreover, under higher resolution, the seemingly continuous bands turn out to consist of closely spaced sharp lines—transitions involving different rotational states (Fig. 9b). Just as in the case of the infrared vibration-rotation spectra

²²² Hund (1927, p. 117).

²²³ Moments of inertia can be inferred from the vibration-rotation spectra discussed in Sect. 6. However, these vibration-rotation spectra, which do not involve electronic transitions, are seen only in molecules that, like HCl , have nonzero electric-dipole moments.

²²⁴ Brand (1995), Fujisaki (1983a,b), Assmus (1991, 1992a,b), and McGucken (1969, Chapter III)

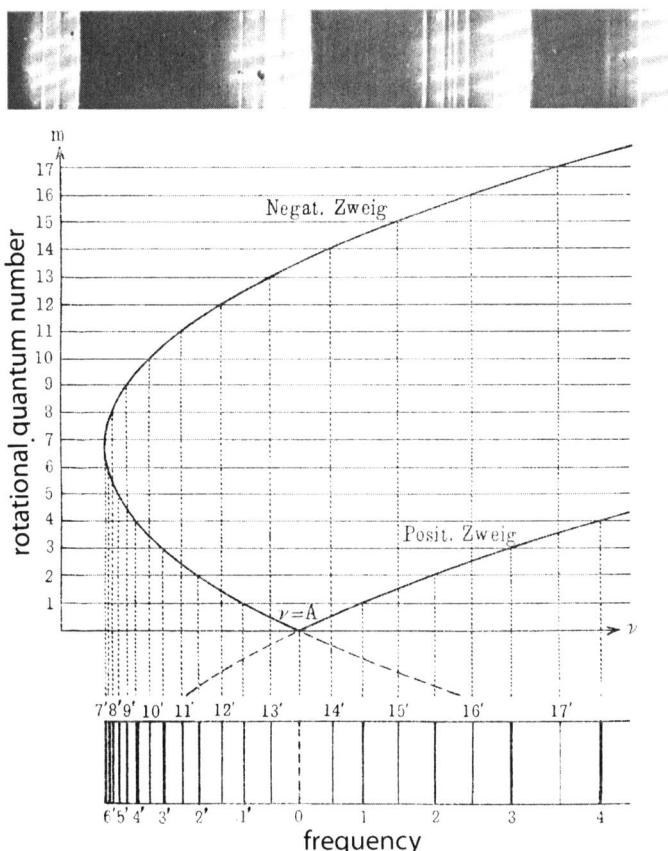


Fig. 9 **a** Top is a portion of the band spectrum of molecular nitrogen, from Foote and Mohler (1922, p. 192A). **b** Bottom is a graph of the rotational structure of a band, called a Forrat diagram, from Sommerfeld (1922, ch. 7, Sect. 3). Note how the lines of one branch not only become more closely spaced, as in Fig. 5, but reach a sharp head (shown in Fig. 9a) and then reverse direction

discussed in Sect. 6 (which do not involve electronic transitions), the spacing of these lines allowed the calculation of moments of inertia.

The differences between moments of inertia in different electronic states are, however, much larger than those that accompany the variable spacing of lines in vibration-rotation spectra. As a result, the frequencies of one “branch”—the frequencies of rotational lines on one side or the other of the central vibrational state—typically reach a sharp “head” at a particular frequency and then reverse direction (Fig. 9b). The data analysis was correspondingly difficult—spectroscopists had to determine which lines corresponded to which branches, taking into account the possibility of overlapping and missing lines.²²⁵

These difficulties pale in comparison to those involved in the measurement and interpretation of “the many-lined spectrum of hydrogen.” In addition to the better-known

²²⁵ Ruark and Urey (1930, esp. Chapter 12), Birge (1926), and Herzberg (1950).

and comparatively simple spectrum of atomic hydrogen, experiments on hydrogen show thousands of lines in the visible and ultraviolet. These lines are widely spaced and do not show diffuse bands or band heads, but were nevertheless associated with molecular hydrogen.²²⁶ By 1913, the American spectroscopist Gordon Fulcher had found two groups of lines that suggested the regularities found in band spectra.²²⁷ But detailed interpretation proved difficult and controversial. By early 1926, a dizzying array of competing and mutually exclusive approaches attempted to explain both these “Fulcher bands” and more recently measured lines.

Not surprisingly, the resulting estimates of the moment of inertia for hydrogen, some of which are given in Table 1, were uncertain—in retrospect, it is surprising that they were compared so widely to values inferred from specific-heat models. One early and indirect estimate was based on the ratio of line spacings in cyanogen and the Fulcher bands.²²⁸ Other, more direct estimates followed, but by 1926 the consensus suggested by Table 1 was breaking down, with some analyses suggesting moments of inertia for hydrogen up to an order of magnitude larger.²²⁹

To make matters worse, none of these lines had been seen in absorption. As a result, nothing was known of the moment of inertia of hydrogen in the ground state, so that as Schrödinger and others had pointed out, spectroscopic values could not be compared directly to those inferred from models for the specific heat of hydrogen. Indeed, hydrogen was notorious for its lack of an absorption spectrum in the far ultraviolet, the region in which both atomic and molecular transitions to the ground state were anticipated. Theodore Lyman, who had pioneered the study of far-ultraviolet spectroscopy, observed in 1914 that: “the transparency of hydrogen [is] uncommonly great. Upon this observation is based the procedure of washing vacuum spectroscopic apparatus with this gas.”²³⁰ His observation reminds us that air absorbs strongly in the ultraviolet, so that spectroscopy must be done under a vacuum; as Lyman ruefully noted in 1922:

The spectroscopy of the extreme ultra-violet combines all the difficulties inherent in the nice adjustment of delicate optical apparatus with those which accompany the production and maintenance of high vacua in metallic containers of large volume.²³¹

If anything, Lyman understated the difficulties. The preparation of photographic plates was an art. The source could not be separated from the spectrometer—even quartz and fluorite windows were far too absorptive at the shortest wavelengths. It was difficult to find sources that emitted a uniform, continuous spectrum for absorption spectroscopy. And so on. Given this experimental complexity, ultraviolet spectroscopy

²²⁶ Sommerfeld (1922, Chapter IV, Sect. 2).

²²⁷ Fulcher (1913).

²²⁸ Sommerfeld (1922, Chapter 7, Sect. 5).

²²⁹ Van Vleck (1926b, esp. Section 3), Birge (1926, pp. 209–214).

²³⁰ Lyman (1914, p. 70). This book contains a detailed description of the sophisticated apparatus and experimental procedure that Lyman had developed.

²³¹ Lyman (1922, p. 162).

developed slowly. Lyman reported the first two lines of his series in atomic hydrogen only in his 1914 book, and the third a year later. He did not see them in absorption until 1926.²³²

The spectrum of molecular hydrogen in the ultraviolet presented similar challenges. Lyman observed in 1914 that, “Hydrogen surpasses all other gases in the wealth and strength of [emission] lines” in the ultraviolet, and immediately added that this spectrum “has defied analysis up to the present time.”²³³ A few pages later, he reported that measurements in which traces of hydrogen were mixed with argon produced a much less complex spectrum, in which he identified five band-like groups of lines.²³⁴ But neither he nor anyone else attempted an analysis.

Thus, although some physicists tried to justify specific-heat models for hydrogen by comparing them to moments of inertia drawn from molecular spectra, others were less sanguine. Van Vleck, for example, after a careful and knowledgeable discussion unsurprising for a student of Kemble, concluded glumly that:

At any rate the hydrogen secondary spectrum is so complicated and difficult to interpret that it does not as yet appear to furnish any conclusive evidence against any of the various specific heat curves ...,²³⁵

although he added enigmatically that:

It is quite probable, however, that spectroscopists of the ultra-violet will soon be able to supply the moment of inertia of the normal state of the hydrogen molecule and so definitely determine the correct value for use in calculating specific heats.²³⁶

The American spectroscopist Raymond Birge also gave a careful summary in the 1926 National Research Council review of molecular spectra, and was if anything even more pessimistic:

A number of investigators are now working on the hydrogen spectrum, and many papers on the subject have appeared during the past few years; but as the conclusions of various investigators are very conflicting, even in regard to the most fundamental points, we shall merely summarize as briefly as possible the main points at issue....²³⁷

²³² Lyman (1914, p. 78), Lyman (1915, 1926). Lyman may have seen the first of these lines, at 1,216 Å, in Lyman (1906), where it is listed in a table of “Lines of unknown origin, probably due to hydrogen.” For an overview, from a physicist’s perspective, see Tousey (1962).

²³³ Lyman (1914, pp. 74–75).

²³⁴ See Ruark and Urey (1930, pp. 503–504) for a discussion of the collision processes involved.

²³⁵ Van Vleck (1926b, p. 996).

²³⁶ Van Vleck (1926b, p. 996). See also Van Vleck (1926a, pp. 101–102). Van Vleck almost certainly learned of the forthcoming developments in spectroscopy from correspondence with Gerhard Dieke, who by 1925 had moved from Leiden to Berkeley and was studying this problem for an experimental Ph.D.; see Dieke to Van Vleck, 9 October 1925 and 1 May 1926, AHQP, microfilm reel 49.

²³⁷ Birge (1926, p. 209).

It was thus a very big deal indeed when in August, 1926, John Joseph Hopfield and Gerhard Dieke, at the University of California in Berkeley, measured numerous bands of molecular hydrogen in both emission and absorption. They sent a preliminary report to *Nature* within 24 h, as Raymond Birge excitedly reported to Kemble later that month. Other, more detailed reports followed shortly.²³⁸

As an undergraduate, Hopfield had met Birge at Syracuse University, and had followed him to California. He completed his Ph.D. degree in 1923 in ultraviolet spectroscopy under the direction of E. Percival Lewis, but with the close cooperation of Birge, and went on to join the Berkeley faculty. Birge was enthusiastic in his support. In a 1929 letter to Van Vleck, he exclaimed that Hopfield "is doing probably the best vacuum spectroscopy of anyone in the world."²³⁹

Dieke had been a student of Ehrenfest in Leiden, where he had earned a master's degree (*Doctorandus*). He had already published several widely read theoretical papers on molecular spectroscopy and one on the specific heat of hydrogen. He had come to California in 1925 intending to study the ultraviolet bands of hydrogen, as he related to Kemble in a May 1926 letter.²⁴⁰ His work with Hopfield was also the subject of his Ph.D. dissertation. Their collaboration was not always smooth; Birge tells us that "anyone who knew these two personally could guess that such a joint effort would not last very long." In fact, Birge became Dieke's advisor, and must have managed somehow to smooth over troubled waters.²⁴¹

Exactly what factors that led to their success is unclear. Among the possibilities were the use of Lyman's new method of generating a continuous ultraviolet source for absorption measurements; the use of two separate vacuum systems, so that the discharge tube and the spectrometer could be maintained at different pressures; Hopfield's new methods of preparing films; and observations over a wide range of pressures, as well as the use of the simpler spectrum Lyman had found using a trace of hydrogen in an argon atmosphere to guide the interpretation of more complex spectra in increasingly pure hydrogen.

In his May letter to Kemble, Dieke had said that although he had not yet succeeded in developing a suitable continuous source for absorption measurements, he had seen numerous bands in emission. By August, the experimental obstacles had been overcome. Dieke and Hopfield's results were stunning. They identified roughly 50 separate bands, organized into a ground state (called *A*) and two excited electronic states (*B* and *C*). Each electronic state contained numerous vibrational states; and each vibrational state contained numerous rotational states. Some dozen bands, involving transitions from either *B* or *C* to *A*, were measured in both absorption and emission. They identi-

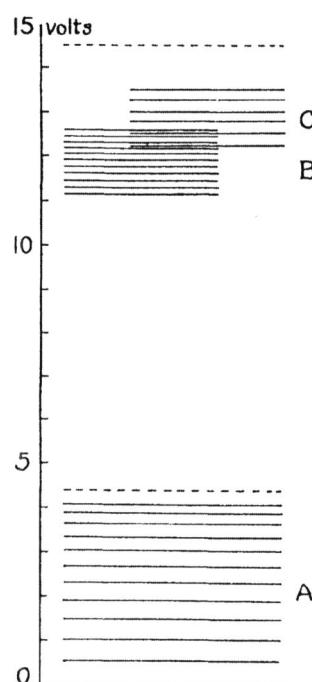
²³⁸ Dieke and Hopfield (1926a,b, 1927), and Birge to Kemble, 26 August 1926, AHQP microfilm reel 50. Birge also asked Kemble, perhaps a bit apprehensively, if Lyman had also seen absorption bands. Birge added a note in proof to Birge (1926, pp. 214–215) reporting these developments.

²³⁹ Birge to Van Vleck, 15 May 1929, as quoted in Birge (1966–1975?, Vol. 2 Chapter 7, p. 18).

²⁴⁰ Dieke to Kemble, 31 May 1926, AHQP microfilm reel 51. See Van Vleck (1926b) and Birge (1926) for full citations.

²⁴¹ See Birge (1966–1975?, Vol. 2, Chapters 7 and 8) for the material on Hopfield and Dieke. For Hopfield, see also the oral interview with Birge conducted in May 1960 by Edna Daniel, for the Regional Cultural History Project of the University of California, on file and available on-line at The Bancroft Library, University of California, Berkeley.

Fig. 10 Dieke and Hopfield’s (1927) energy-level diagram showing the ground electronic state *A* and two excited states *B* and *C* in molecular hydrogen. The lines represent vibrational states within each electronic state. Not shown are the even more closely spaced rotational states associated with each vibrational state



fied the bands Lyman had found in 1914 as transitions from the $n = 3$ vibrational state of *B* to the ground state *A*. They summarized all of this information in an energy-level diagram (shown in Fig. 10). They did not, however, analyze the rotational structure of these bands, saying only that “a discussion ... is reserved for another paper.”

Earlier in 1926, Enos Witmer, who was working for Kemble as a National Research Council fellow after completing his Ph.D. at the University of Pennsylvania in 1924, reported seven additional bands that Lyman had measured in emission in 1925 but had not published.²⁴² Witmer showed that these bands (also a subset, it transpired, of Dieke and Hopfield’s *B*-to-*A* transitions) all began on the same vibrational state; and he strongly suspected that they ended on the ground state (or “normal” state, as it was often called). He gave a preliminary analysis of the rotational structure, but made no attempt to calculate a moment of inertia. Witmer abandoned plans for further work on these bands after learning of Dieke and Hopfield’s more comprehensive results, according to a letter from Kemble to Dieke in June, 1926.²⁴³

Yet another experiment appeared on the scene that summer. In August 1926, Sven Werner, a spectroscopist working at Niels Bohr’s institute in Copenhagen, reported

²⁴² Witmer (1926a,b). Witmer spent most of his subsequent career in the Physics Department at the University of Pennsylvania. In 1928, he was a coauthor with Eugene Wigner of an important paper on molecular symmetries and molecular spectra, Wigner and Witmer (1928).

²⁴³ Kemble to Dieke, 14 June 1926, AHQP microfilm reel 51. Kemble noted that he had been hoping to analyze the Lyman bands for some time, but that there had been no opportunity to do so until Witmer appeared on the scene. Dieke had previously told Kemble that he had not known of the Lyman bands until he saw Witmer’s first paper, well after his own work was underway (footnote 240).

finding a number of new emission bands in the far ultraviolet that turned out to correspond to Dieke and Hopfield's *C-to-A* transitions.²⁴⁴ Werner by his account had stumbled across these lines in a study of the ultraviolet spectra of lithium and other elements, in which the hydrogen lines at first "proved to be a very distracting impurity...." His analysis was at best preliminary; at one point he said flatly that, "No satisfactory explanation of the bands has yet been found." He nevertheless undertook a provisional rotational analysis, and without giving much detail, reported a value for the moment of inertia in the ground state in the range of 2 to 3×10^{-41} gm cm². This value did not, however, hold up.

Werner's paper serves to remind us that that in spite of its name, Bohr's Institute for Theoretical Physics had from its earliest days supported an active and well-equipped spectroscopy laboratory.²⁴⁵ It is therefore no surprise to find Takeo Hori, a young Japanese spectroscopist visiting Europe on a grant from the Japanese government, writing to Bohr from Berlin, in May 1926, giving an account of himself, and asking to visit the Copenhagen laboratory. To Hori's delight, Bohr invited him to come the following September, since the laboratory would be closed over the summer for reconstruction. Hori promptly accepted: "Now that my destination is settled, I can freely enjoy the coming three months.... I shall be in Copenhagen by the end of August."²⁴⁶

At Bohr's suggestion, Hori took on the task of remeasuring and reanalyzing the Werner bands. He also reanalyzed the new Lyman bands recently published by Witter. And he did so in the context of the path-breaking paper of Dieke and Hopfield, which appeared while Hori's own work was in progress. Hori's work took nearly a year; his paper was submitted to the *Zeitschrift für Physik* in July 1927.²⁴⁷ Hori's acknowledgments, not only of Bohr, but also of Hund, David Dennison, Erwin Fues, and Yoshio Nishina (all of whom were then in Copenhagen), suggest that these developments were widely discussed at Bohr's Institute.

Hori carefully described his extensive reanalysis of both the Lyman and Werner bands, and in the process gave the first detailed analysis of the rotational structure of the H₂ ultraviolet bands. The resulting value for the moment of inertia of a hydrogen molecule in the ground state, 4.67×10^{-41} gm cm², was more than triple Hund's value. Hori also saw rotational lines of alternating intensity in the Werner bands (though not in the Lyman bands),²⁴⁸ and, as he pointed out in a long footnote, his observations directly contradicted Hund's assumptions:

[Hund] obtains $\beta = 2$, that is, the ... [even] rotational states of the ground term have approximately twice the statistical weight as the ... [odd] rotational states. This does not agree with the result obtained from the analysis of the bands, which makes it necessary to adopt a value $\beta < 1$.

²⁴⁴ Werner (1926).

²⁴⁵ See for example Bohr's speech at the dedication of his Institute on 3 March 1921, in Bohr (1972–1996, Vol. 3, 293–301, esp. p. 296); see also Robertson (1979, esp. pp. 41–47). A photograph of Takeo Hori is on p. 128.

²⁴⁶ Hori to Bohr, 9 May 1926; Bohr to Hori, 19 May 1926; Hori to Bohr, 21 May 1926; AHQP, Bohr Scientific Correspondence, microfilm reel 12.

²⁴⁷ Hori (1927).

²⁴⁸ Alternating intensities in the Lyman bands were eventually seen; see Richardson (1934, p. 89).

In other words, Hund’s choice ($\beta = 2$, symmetric total wave function) implied that transitions between symmetric rotational states should be brighter; Hori’s observations showed just the opposite: transitions between antisymmetric rotational states are brighter, implying $\beta < 1$ and an antisymmetric total wave function.

As the quotation at the end of Sect. 10 shows, Hund was puzzled by Hori’s results. I do not know how complete those results were in February 1927, when Hund submitted his paper, but Dennison may have known the previous December that a reanalysis of the Werner bands was yielding a considerably larger moment of inertia than Werner originally had reported. Whatever the case, Hund’s failure to discuss Hori’s results at more length remains a mystery.

The reception of Hori’s remarkable experimental work owed something to its location in Copenhagen, where it was immediately relevant to Heisenberg’s and Hund’s theoretical work on identical particles and the hydrogen problem. The importance of this connection may be seen in the reception (or lack thereof) of a parallel analysis by the British physicist Owen W. Richardson. Richardson, who would win the Nobel Prize in 1928 for his work on thermionic emission, published in 1924 the first in a long series of papers on the many-lined spectrum of hydrogen, primarily in the visible. His work eventually led to a more complete understanding and integration of the visible and ultraviolet spectrum of molecular hydrogen, summarized in his 1934 book, *Molecular Hydrogen and Its Spectrum*.

In 1926 and 1927, drawing on his own work in the visible, and on that of Werner, Witmer, and Dieke and Hopfield, Richardson used an indirect method to estimate the moment of inertia of a hydrogen molecule in the ground state, and found a value about the same as Hori’s. Nevertheless, Hori’s result was (and still is) almost exclusively cited. Richardson seemed a little put out. In his book, he spent several pages describing his own results, and concluded dryly that: “Hori’s value..., got from his analysis of the Werner and Lyman bands, was also published about the same time.”²⁴⁹

12 David Dennison and the specific heat of hydrogen

In 1924, David Dennison completed his Ph.D. at the University of Michigan under the direction of Walter Colby and Oskar Klein, the latter newly arrived from Niels Bohr’s institute in Copenhagen. From Klein, Dennison learned the latest developments in quantum theory at firsthand. Harrison Randall, whom we met earlier as Elmer Imes’s dissertation supervisor, was continuing to build the program in molecular spectroscopy at Michigan. Dennison’s thesis on the structure and infrared spectrum of methane continued that tradition. Perhaps more surprising, his was the first theoretical dissertation at the University of Michigan. Dennison later said that Randall was “very uneasy” about this prospect, but that “there was no putting me off.”²⁵⁰

²⁴⁹ Richardson (1934, p. 285). Richardson’s book gives full citations of his earlier work.

²⁵⁰ Thomas S. Kuhn, interview with David Dennison, AHQP, Session 1 (27 January 1964), p. 11. For more on Dennison see Crane (1980), and Rigden (1990).

Bohr visited Michigan late in 1923, during his first visit to the United States. That visit resulted in an invitation for Dennison to come to Copenhagen. Dennison jumped at the chance:

At this time it was decided I would go to Copenhagen. Just how I was to go, this was another question. But I was absolutely positive I was going. There was just no question.²⁵¹

Dennison set out for Copenhagen in the fall of 1924 and stayed through the spring of 1926; he thus saw the birth of matrix mechanics at firsthand. He continued to work on molecular spectroscopy; one paper that combined these themes, suggested to him by Hendrik Kramers, gave a detailed treatment of both the rigid and gyroscopic rotator in matrix mechanics. In later years, he proudly recalled that it was the first paper on matrix mechanics published in the *Physical Review*.²⁵² At some point, he became interested in the specific heat of hydrogen. Heisenberg later recalled talking to him about it,²⁵³ and Dennison himself recalled that:

Oh yes, I certainly had thought about the specific heat much earlier, and how it would be related to the spectra and to the moment of inertia.

[It] was a problem I was thinking about ... some [problems] came out and some didn't, and this was one that hadn't come through.²⁵⁴

Dennison returned to the United States in the summer of 1926, but that fall set sail again for Europe, this time to work with Erwin Schrödinger in Zurich. Just as his visit was ending in December, he submitted a two-page letter to *Nature* on the rotation of homopolar (identical nuclei) molecules, which appeared at the end of February 1927.²⁵⁵ Dennison later described this article as "showing my state of confusion more than anything else."²⁵⁶ His assessment was far too harsh. The article showed him puzzling over both the specific heat of hydrogen and the lines of alternating intensity, and embarking on an insightful if as yet incomplete train of reasoning that bore fruit only a few months later.

Dennison began by recalling John C. Slater's argument, about a year earlier, that if one used Sommerfeld's quantum condition, Eq. (24), to quantize the angular momentum of homopolar molecules, the angular period should be only 180° instead of a full 360°, since the molecule "returns after half a revolution to a state which cannot be told from its initial state...." Slater's condition implied that every other rotational line should be missing, as was suspected to be the case for molecular helium. He speculated

²⁵¹ Thomas S. Kuhn, interview with David Dennison, AHQP, Session 2 (28 January 1964), p. 8. Dennison described turning down one fellowship offer that would have required him to remain in the United States.

²⁵² Dennison (1926), and AHQP interview (footnote 250), session 2 (28 January 1964), p. 16.

²⁵³ Heisenberg, AHQP interview (footnote 164), session 6 (19 February 1963), p. 15. Heisenberg is, however, vague about the content of his conversations, although he did recall "many discussions with Dennison on the specific heat question." Dennison also recalled his conversations with Heisenberg; see Dennison, AHQP interview (footnote 250), session 3 (30 January 1964), p. 4.

²⁵⁴ Dennison AHQP interview (footnote 250), session 3 (30 January 1964), p. 15.

²⁵⁵ Dennison (1927a).

²⁵⁶ Dennison (1974, p. 1053).

that a “continuous kind of transition to the case of the non-symmetrical rotator” might account for the lines of alternating intensities seen in molecular nitrogen. A detailed theory along these lines might well have emerged in the old quantum theory, had not modern quantum mechanics intervened.²⁵⁷

Dennison took up Slater’s suggestion in the language of Schrödinger’s new wave mechanics, in which he was by now fluent. The wave functions for the rigid rotator are the spherical harmonics, which are either odd or even depending on whether the rotational quantum number is odd or even, when a molecule undergoes a rotation of 180°—equivalent, of course, to an exchange of nuclei. Dennison pointed out that if the wave function was single-valued (or even, as we would say today) under a 180° rotation, then only *even* rotational quantum numbers would be allowed. But as he also pointed out, such a conclusion appeared inconsistent with the spectrum of molecular helium. Just as bad, the specific heat of hydrogen calculated with only even rotational quantum numbers showed the peak that had puzzled theorists for years.

Dennison suggested as an alternative the requirement that the absolute square of the wave function be single-valued, arguing that such an assumption is: “more nearly in accord with the spirit of the new mechanics, since the function $\psi\bar{\psi}$ seems to represent the electrical density, whereas the function ψ alone has no such physical meaning.”²⁵⁸ Under this assumption either odd or even solutions would be admissible. However, as he went on to state without proof, the solutions for odd and even rotational quantum numbers were: “each complete in themselves and admit of no intercombination, [and] seem to correspond respectively to the symmetrical and antisymmetrical solutions found by Dirac and Heisenberg....” In short, Dennison had followed a path similar to Heisenberg. But without the latter’s assumption of a nuclear spin that allowed weakly combining odd and even rotational states, he concluded that only one set might actually exist. Dennison thus seems to have come across a special case of what would become a much more general argument: the invariance of $\psi\bar{\psi}$ under exchange of indistinguishable particles implies that ψ itself must be either symmetric or antisymmetric, a derivation now found routinely in textbooks, but as far as I know, still unknown late in 1926.²⁵⁹

Dennison stated without giving any detail that odd rotational quantum numbers were consistent with the helium bands.²⁶⁰ He also calculated the specific heat of

²⁵⁷ Slater (1926, p. 555); see also Ehrenfest and Tolman (1924) and Birge (1926, pp. 204–209). Kemble, with whom Slater had studied at Harvard, praised Slater’s approach in letters to Van Vleck, 15 November 1925, and to Raymond Birge, 26 March 1926, AHQP microfilm reel 50.

²⁵⁸ Note that Dennison was following Schrödinger’s interpretation of $|\psi|^2$. If he knew of Max Born’s probabilistic interpretation that had appeared in the summer of 1926, he said nothing about it.

²⁵⁹ Dennison’s later accounts do not do justice to this argument. His discussion of this paper in his AHQP interview (footnote 250), session 3 (30 January 1964), pp. 10–11, is not very detailed, and his recollections of it did not seem to be sharp. He went into more detail in both an unpublished talk at the University of Michigan in the late 1960s (Bentley Library, University of Michigan, Dennison Archive, Box 2) and in Dennison (1974); but there his discussion centered on a later section of the paper that outlined a solution of Schrödinger’s equation for a rigid rotator involving half-quantum numbers. That section is, as far as I can tell, unrelated to the argument outlined above.

²⁶⁰ The situation is in fact more complex. Hund (1927) made a start, but a full theory of the alternating intensity bands required a better understanding of molecular symmetries that developed over the next few years. See Mulliken (1931, pp. 146–155).

hydrogen using only odd states, and found that the specific heat showed a steady rise, with no peak. His value for the moment of inertia using only odd states was 6.7×10^{-41} . By way of confirmation, he referred to Sven Werner's discovery of new bands in the far ultraviolet, for which he quoted a moment of inertia in the ground state of 6×10^{-41} —much larger than the value that Werner had reported and larger even than Hori's still-unpublished value. Perhaps Dennison had been in touch with the spectroscopists in Copenhagen, and knew that Werner's published estimate was being superseded by Hori's.

Thus, motivated by his discovery that odd and even rotational states might be independent and noncombining, Dennison had for the first time calculated the specific-heat curve for odd and even rotational states separately and had seen their very different behavior. He stated—incorrectly—that the specific heat calculated with only the odd states gave a reasonable fit to the data, and closed by promising “a more detailed paper covering the calculations.”²⁶¹

Dennison's short letter received mixed reviews. He had sent the manuscript to Bohr in Copenhagen, and in January 1927 got in return two letters from Oskar Klein. Klein said that he and Bohr had forwarded the paper to *Nature*, even though they had reservations about his assumption regarding $\psi\bar{\psi}$. Klein also told Dennison about Heisenberg's December 1926 paper, which Klein held out as “the only solution ... which is rational from the point of view of quantum mechanics.”²⁶² He promised to send a copy as soon as proofs became available, and suggested that Dennison might want to make changes in proof to his own paper.

Given this discouraging reaction, Dennison must have been pleased to receive a short letter from Ralph H. Fowler, whom he had come to know in Copenhagen, written almost immediately after Dennison's note had appeared. Fowler expressed his delight with the paper, agreed strongly with Dennison's suggestion that $\psi\bar{\psi}$ should be single-valued, and concluded by urging him to visit Cambridge before he returned home.²⁶³

The spring of 1927 found Dennison in Cambridge, after a visit to Munich and a second stay in Copenhagen where, as he later recalled, he learned the details of Hori's experiments and analysis. In Cambridge, he turned again to the specific heat of hydrogen, and this time, he succeeded. As he later explained:

²⁶¹ In his February paper, Hund (1927) had also plotted the contribution to the specific heat from only the odd states, perhaps inspired by Dennison's *Nature* paper (1927a), which he cited in another connection. He found a value for the moment of inertia about the same as Dennison's, but also showed that the odd states alone did not adequately describe the data. Under these circumstances, it seems hard to imagine that Hund did not have an inkling of Hori's higher value for the moment of inertia—it makes his cryptic reference, quoted at the end of Section 10, seem all the more mysterious.

²⁶² Klein to Dennison, 11 January and 22 January 1927, AHQP, microfilm reel 59. The quotation is from the second letter.

²⁶³ Fowler to Dennison, 27 February 1927, AHQP, microfilm reel 59.

Fowler asked me to give three lectures to his graduate class.... I could see that I was running out of material for the third lecture ... and it occurred to me to take another crack at the problem of the specific heat of hydrogen.²⁶⁴

By this time, Dennison had seen both Heisenberg’s and Hund’s papers from the previous December and February. He knew, therefore, that the introduction of nuclear spin allowed weakly combining odd and even states, contrary to his assumption in his *Nature* paper. He also had seen Hori’s as yet unpublished results, including the new moment of inertia, and the observation of rotational lines of alternating intensity implying $\beta < 1$, in contrast to Hund’s assumption of a symmetric total wave function and hence a $\beta > 1$.

Dennison pointed out that Hori’s results ruled out Hund’s $\beta = 2$ and his much smaller moment of inertia. Dennison added that if $\beta = 1/3$, Hund’s theory led to an impossible curve, with a sharp peak rising well above the equipartition value. In other words, he knew that no value of Hund’s β would work as long as the ortho and para terms could combine, however weakly. Dennison’s conclusion appeared almost inevitable:

[The] difficulties ... may lie in the assumption that the symmetrical and anti-symmetrical terms can combine....

Let us make the assumption that the time of transition between a state symmetrical in the rotation, and an antisymmetrical state is very long compared with the time in which the observations of the specific heat are made.²⁶⁵

Under these circumstances, one must treat hydrogen as a mixture of parahydrogen and orthohydrogen in the fixed, room-temperature ratio. Dennison said that Hori’s alternating intensity measurements implied the ratio $\beta \approx 1/3$, that is, three parts orthohydrogen (odd rotational states) to one part parahydrogen (even rotational states). (Hori had not given a specific value, noting only that β must be less than one.²⁶⁶)

As additional evidence, Dennison pointed out that only the even rotational states led to a peak, and therefore one would expect the odd states to contribute more strongly, in agreement with Hori’s observations. He did not publish a graph (see Fig. 11),²⁶⁷ but a table showed that a ratio of 3 parts ortho to one part para led to “a specific heat curve which follows the observed curve to within the errors of observation, and that moreover the constants ... are in good agreement with the values ... found in the band spectrum of H_2 . ”

²⁶⁴ Dennison (1974, p. 1054). This story sounds too good to be true; but it is confirmed in a contemporary letter, Dennison to Bohr, 2 June 1927, AHQP, Bohr Scientific Correspondence, microfilm reel 9, in which Dennison told Bohr about his new result.

²⁶⁵ Dennison (1927b, p. 484).

²⁶⁶ Tomonaga (1997, p. 73), says that Hori had told Dennison that the intensity ratio was about 3:1, but gives no source. I have not seen this account elsewhere; but Tomonaga’s book is historically sensitive, and, as it turns out, Hori was Tomonaga’s brother-in-law!

²⁶⁷ Dennison did make a careful graph, which, as he reported in the late 1960s, appeared nearly unchanged in Fowler’s statistical mechanics textbook; see Fowler (1929, p. 54; 1936, p. 83). See Dennison’s unpublished notes for a talk given circa 1968 at the University of Michigan (Bentley Library, University of Michigan, Dennison Archive, Box 2, p. 15).

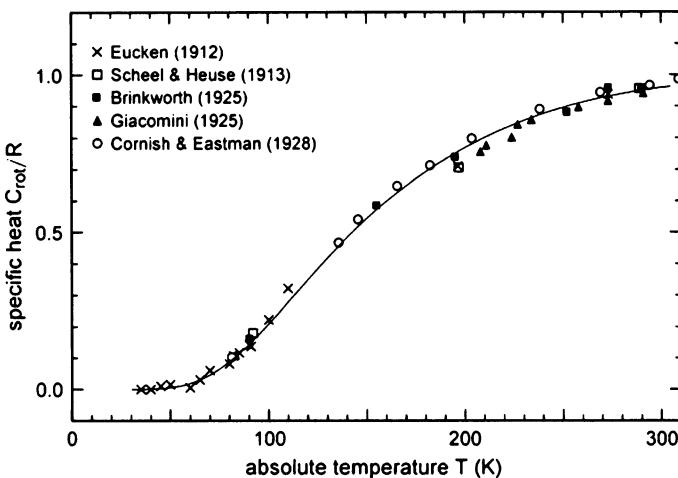


Fig. 11 Specific heat curve of Dennison (1927b). Dennison did not include this graph in his article. I have shown the data of Cornish and Eastman (1928), which did not appear until a year later

Up to this point, Dennison had not explicitly mentioned the implications for spin and total wave-function symmetry, though he surely understood them; he could have arrived at his 3:1 ratio in no other way. But in response to a suggestion from Bohr,²⁶⁸ to whom he had sent a draft, he added the comment that “the ratio of 3 to 1 of the antisymmetrical and symmetrical modifications of hydrogen ... is just what is to be expected if the nuclear spin is taken equal to that of the electron, and only the complete antisymmetrical solution of the Schrödinger wave equation allowed.” Many years later, he said that, “Somehow this point had seemed so obvious to me that it had not seemed worth belaboring.”²⁶⁹

In his letter to Dennison, Bohr expressed his delight that a solution to this longstanding problem had finally been found. Hori, writing to Bohr from Tübingen, was equally pleased to hear that his experimental results and analysis had found such striking confirmation.²⁷⁰ As we have seen, Heisenberg, Hund, and Dennison, as well as Hori and the Copenhagen spectroscopists, had all been in Bohr’s institute during these years, talking to one another and setting the stage for Dennison’s discovery. We should not forget that Van Vleck, following developments at a distance in Minneapolis, had not seen the significance of Heisenberg’s first helium paper. And Richardson’s 1926–1927 estimate of the moment of inertia of hydrogen drew almost no notice—even today, it is hardly ever cited. Mara Beller has argued that the dialogue among the leading actors was central to the discovery and interpretation of modern quantum mechanics.²⁷¹ It was equally important in the story of the specific heat of hydrogen.

²⁶⁸ Bohr to Dennison, 9 June 1927, AHQP, microfilm reel 59.

²⁶⁹ Dennison (1974, p. 1056).

²⁷⁰ Hori to Bohr, 19 July 1927, AHQP, Bohr Scientific Correspondence, microfilm reel 12.

²⁷¹ Beller (1999).

13 The experimentalists have the last word

From the outset, Dennison’s theory seemed enormously plausible. But were there in fact two varieties of molecular hydrogen? The existence of orthohelium and parahelium were supported by well-established spectroscopic measurements of the noncombining singlet and triplet term series. But in view of the difficulties in measuring the “many-lined spectrum” of hydrogen, some years were to pass before molecular spectroscopists could confidently assert the existence of similar singlet and triplet term series in hydrogen.²⁷² Nevertheless, Dennison’s solution to a prominent and long-standing puzzle in quantum theory gave rise to an outburst of experimental activity.

In contrast to helium, the thermal properties of orthohydrogen and parahydrogen should be noticeably different, as Dennison’s discovery of different specific-heat curves for odd and even rotational states might suggest. Experimentalists immediately set out to measure those properties. Kemble, for example, hoped to have a student maintain a sample of hydrogen gas at liquid-air temperatures for a week or so, and see if the specific heat changed.²⁷³ Edward U. Condon made a similar suggestion to experimentalists at the University of California, only to discover, as William F. Giauque and Herrick L. Johnston reported, that the apparatus used by Robert E. Cornish and Ermon D. Eastman had already been “completely dismantled”; and measurements of the triple point after keeping hydrogen at the temperature of liquid air for over six months proved inconclusive.²⁷⁴

A group of German physical chemists centered on Fritz Haber’s Kaiser Wilhelm Institute for Physical Chemistry in Berlin was more successful. This group very much included Arnold Eucken, since 1919 a professor at the Technical University [*Technische Hochschule*] in Breslau, whose interest in the specific heat of hydrogen had never waned since his publication of the first measurements in 1912.²⁷⁵ Reports of the first successful measurements appeared in two brief articles on the same page of the 15 March 1929 issue of *Die Naturwissenschaften*. In the first, Karl-Friedrich Bonhoeffer and Paul Harteck, two young physical chemists at Haber’s institute, announced a new and innovative technique. Instead of the heat capacity, they measured the thermal conductivity of the gas by recording the temperature of a platinum wire in a container filled with hydrogen. The thermal conductivity is directly proportional to the specific heat, but thermal conductivity measurements can be made more quickly and conveniently. Thus a higher thermal conductivity corresponded to the larger specific heat expected at most temperatures for parahydrogen.²⁷⁶

²⁷² Richardson (1934, p. 163).

²⁷³ Kemble to Birge, 17 January 1928, AHQP microfilm reel 50.

²⁷⁴ Giauque and Johnston (1928); see also Cornish and Eastman (1928).

²⁷⁵ See, for example, Eucken (1914, Appendix), Eucken (1920a,b, 1926). This list is not exhaustive.

²⁷⁶ Bonhoeffer and Harteck (1929). This short note was followed by several more detailed reports. For a full bibliography and details of the experiments on the thermal properties of para- and orthohydrogen, see Farkas and Farkas (1934). Bonhoeffer had been a student of Nernst. Harteck had been an assistant with Eucken in Breslau, after having completed his Ph.D. in Vienna. For more on both, see the thumbnail biographies in Hentschel (1996, Appendix F, pp. xix and xxxi). See also Jaenicke (1957), Harteck (1960), Farkas (1989), and the biography of Bonhoeffer at the web site of the Max-Planck-Institut für biophysikalische Chemie, <http://www.mpibpc.mpg.de/kfb/index.html>.

Bonhoeffer and Harteck made their initial experiments at the temperature of liquid air. They found that at low pressures, hydrogen transformed very slowly to the new ortho-para ratio expected at this lower temperature (about 1:1). At higher pressures (several hundred atmospheres), however, the transformation (presumably accelerated through collisions) proceeded much more rapidly, achieving within a week the new equilibrium concentration. Equally important, they discovered that the presence of catalysts strongly accelerated the transformation. In perhaps their most striking result, they found that hydrogen adsorbed on activated charcoal at liquid-hydrogen temperatures and then pumped off was transformed in a matter of minutes to the nearly pure parahydrogen expected at this low temperature. If stored carefully without impurities in a glass container, it remained stable for some weeks even at room temperatures.

In the second article, Arnold Eucken took a more direct approach. Using an improved version of his 1912 calorimeter, he and his assistant Kurt Hiller stored hydrogen under high pressure (about 50 atmospheres) for several weeks, periodically measuring its specific heat over the range 90–150 K. After about 2 weeks, their data matched the theoretical equilibrium concentration of 36% parahydrogen, a substantial increase over the 25% found in “ordinary” hydrogen. The crowning touch came in an experiment by Hiller and Klaus Clusius, another student of Eucken who went on to a distinguished career. They prepared a sample of 95% parahydrogen using Bonhoeffer and Harteck’s activated charcoal technique and measured its specific heat up to about 160 K, where the rotational specific heat was roughly 40% higher than the equipartition value seen at room temperature. In other words, their experiment had finally seen the peak in the specific heat of hydrogen that had haunted the imaginations of physicists and physical chemists since Paul Ehrenfest first came across it in 1913.²⁷⁷

In 1932, the discovery of heavy hydrogen (now called deuterium) by Harold C. Urey and his associates led to additional and unexpected evidence for the new quantum-mechanical picture. Urey’s discovery led to an outburst of experiments on the physical and chemical properties of this new isotope.²⁷⁸ In short order, measurements of the lines of alternating intensity in the molecular spectrum of heavy hydrogen showed that its nucleus obeyed Bose–Einstein statistics, and most likely had spin 1. In consequence, in the ground state the ratio of even-to-odd rotational states should be 2:1, instead of the 1:3 ratio in ordinary hydrogen.

Moreover, heavy hydrogen turned out to have an even smaller magnetic moment than ordinary hydrogen, so that transitions between odd and even rotational states should be even less frequent. As Dennison had first discovered, only transitions between even rotational states result in a peak in the specific heat. Hence this new even-to-odd ratio predicted a peak in the specific heat of D₂. The possibility of an HD hydrogen molecule, in which the nuclei are not identical, also became apparent. Its rotational partition function is much the same as in the old quantum theory, with the same prediction of a peak in the specific heat.

²⁷⁷ Eucken (1929), Eucken and Hiller (1929), Clusius and Hiller (1929). Clusius and Hiller’s graph is in Eucken and Hiller (1929). See also Farkas (1935). For more on Clusius, see Hentschel (1996, Appendix F, p. xxi), Eggert (1963), and Schleich (1964). I have been unable to learn anything about Hiller.

²⁷⁸ Urey et al. (1932). For summaries of subsequent developments over the next several years, see Urey and Teal (1935), and Farkas (1935); see also Stuewer (1986).

The German physical chemists once again took the lead. Paul Harteck, along with two former students of Bonhoeffer, Adalbert and Ladislas Farkas, used the same thermal-conductivity techniques that Bonhoeffer and Harteck had pioneered, but adapted so that much smaller samples were needed.²⁷⁹ Their experiments confirmed the expected para-ortho conversion at various temperatures, and provided additional evidence that heavy hydrogen obeyed Bose–Einstein statistics and had spin 1. They also investigated the reaction $H_2 + D_2 \rightleftharpoons 2HD$, confirming earlier estimates of the equilibrium constant for the reaction. These experiments were done at the University of Cambridge in England. The Farkas brothers were Hungarian Jews who had to leave Germany in 1933. They later went on to careers in Israel and the United States. But in 1934, they were at Cambridge, where they were joined by Harteck, who spent a year working with Ernest Rutherford learning nuclear physics. Rutherford assigned Harteck the task of preparing a sample of heavy hydrogen for the laboratory. Ironically, Harteck would use his knowledge of heavy water and isotope separation in the German nuclear program in World War II.²⁸⁰

Arnold Eucken was once more involved in the measurements of the specific heat of HD and D_2 , though this time indirectly. Eucken was by now the head of an institute at the University of Göttingen. The experiments there were done by his former student Klaus Clusius and by Ernst Bartholomé, who had completed his Ph.D. degree at Eucken’s new institute in 1931. Clusius and Bartholomé employed much the same technique that Eucken had pioneered in 1912, and acknowledged Eucken’s support. It turns out to be impossible to obtain samples of pure HD; instead, they worked with two mixtures, one almost entirely D_2 and HD, the other almost entirely H_2 and HD. Since they could calculate the percentages of HD in each mixture from the equilibrium constant of the $H_2 + D_2 \rightleftharpoons 2HD$ reaction, they could find the specific heats of D_2 and HD separately. Their measurements confirmed the expected peaks in both.²⁸¹

14 “Astonishing Successes” and “Bitter Disappointment”

Fritz Reiche had followed the quantum theory of rotating dumbbells from the beginning after receiving his Ph.D. in 1907. He contributed extensively to quantum theory himself, and wrote one of the earliest quantum textbooks. He had watched as (among others) Einstein, Ehrenfest, and Planck, his Ph.D. supervisor, had tackled the specific heat of hydrogen. His own encyclopedic 1919 paper left little enough for others to do in the old quantum theory; later attempts consisted in large part of applying half-quanta to the theory that Reiche had laid out.²⁸² Physicists remained faced with a blatant discrepancy between theory and experiment. They never lost sight of the problem and

²⁷⁹ Farkas and Farkas (1934), Farkas et al. (1934).

²⁸⁰ See Farkas (1989), and Chayut (1994). Harteck and the Farkas brothers remained on good terms; but for a darker and more comprehensive perspective, see Deichmann (1999, esp. pp. 23–26), and for further discussion and bibliography, Hentschel (1996), and Walker (1989).

²⁸¹ Clusius and Bartholomé (1934). For more on Bartholomé, see Schäfer (1973). For a graph of the D_2 data and the theoretical curves, see Fowler (1936, pp. 87–88).

²⁸² Kemble, of course, had developed much the same theory in similar detail in his dissertation two years earlier; but I doubt that anyone besides Van Vleck knew the full scope of what Kemble had accomplished.

talked about it extensively; but, as Schrödinger's 1924 contribution might suggest, they had little idea what to try next. The rotator, at bottom, remained a straightforward textbook problem that offered little scope for innovation. Perhaps for that reason, the founders of modern quantum mechanics, centered on Göttingen and Copenhagen, never took up the problem in the old quantum theory. Recall, for example, how Born, in his 1925 textbook, analyzed most of the pressing problems in quantum theory in great detail, but nevertheless dismissed the specific heat of hydrogen with a few summary paragraphs and a reference to Reiche's 1919 paper.²⁸³ Problems such as the helium atom, the Zeeman effect, and dispersion offered more scope for theoretical speculation. That state of affairs changed only with the advent of modern quantum mechanics in 1925.

Reiche never lost interest in the specific heat of hydrogen. His undated Breslau lecture notes, probably from 1928, contain calculations based on Dennison's paper and a careful graph.²⁸⁴ A year or so earlier, in February 1927, Reiche had written John Van Vleck to acknowledge receipt of copies of Van Vleck's and Hutchisson's papers.²⁸⁵ In that letter, Reiche ruefully observed that neither the gyroscopic model of his student Hans Lessheim, nor Van Vleck's model discarding the lowest energy state seemed likely solutions. But he had little else to offer, apart from a passing reference to Hund's paper—if he saw the promise of Heisenberg's and Hund's new quantum-mechanical treatment of identical particles, he nevertheless said nothing about it. And Van Vleck himself had made no more than a passing reference to Heisenberg's first helium paper.

These reactions help us see why the problem of the specific heat of hydrogen defied solution for so long, despite enormous and wide-ranging theoretical and experimental efforts. Very often the old quantum theory pointed the way, however obscurely, to its successor. For example, the half-quantum numbers first introduced by Heisenberg and Kratzer, and independently by Reiche and Einstein, seemed incomprehensible at first. But they worked, and eventually found a natural explanation in modern quantum mechanics. Such examples as Pauli's “ban of equivalent orbits,” the attempts to understand the statistical mechanics of ideal gases, and approaches such as Slater's show the increased interest in identical particles that emerged during the early and mid-1920s. Slater's theory might eventually have led to a successful explanation of both alternating intensities and the specific heat of hydrogen, though it surely would have had the same empirical and mysterious flavor as half-quanta. All the same, nothing like Heisenberg's and Dirac's new theory of identical particles ever appeared in the old quantum theory; the initial failure of such capable theorists as Reiche and Van Vleck to recognize its central importance shows us just how novel and unexpected it was. Hund and Dennison, by contrast, who witnessed the development of the new quantum mechanics and Heisenberg's theory of identical particles in intimate detail, saw immediately their relevance to the hydrogen problem.

²⁸³ Born (1925, Sect. 12).

²⁸⁴ Fritz Reiche, lecture notes, from Reiche papers, Niels Bohr Library, American Institute of Physics, College Park, MD, Box 7, Folder 2. My estimate of the date is based on a 1928 paper cited in these notes; in addition, Reiche made no mention of either Bonhoeffer and Harteck's or Eucken's 1929 papers.

²⁸⁵ Reiche to Van Vleck, 20 February 1927, AHQP, microfilm reel 59.

This long and complex story, which began with Walther Nernst in 1911 and continued for more than 20 years, gives us a new and complementary perspective on the successes and failures of the old quantum theory and its eventual replacement by modern quantum mechanics. The rotating dumbbell, applied to both molecular hydrogen and molecular spectra, provided much of the early evidence for quantum theory. It also led to a stream of theoretical and experimental discoveries in molecular physics that showed both the possibilities and the limitations of the old quantum theory; and, by showing how the quantum statistics of indistinguishable particles led to the solution of a long-standing problem, it lent additional insight into the nature of today’s quantum mechanics. The story reminds us that the history of early quantum theory extends far beyond its better known applications to atomic physics.

Acknowledgements It is a pleasure to acknowledge the following individuals and institutions: David C. Cassidy, Ronald E. Mickens, Alfons Weber, Roger H. Stuewer, and Anne Lee Bain read earlier versions of this paper and made numerous helpful comments and suggestions. Michel Janssen likewise made many helpful comments and suggestions in the course of numerous stimulating conversations. Jeffrey J. Prentis and William A. Fedak looked through the David Dennison Archive at the Bentley Library at the University of Michigan and sent me copies of relevant documents. Robert W. Seidel lent me his copy of Birge (1966–1975?). I presented preliminary versions of parts of this paper at the annual meeting of the History of Science Society (2005), and at HQ0, HQ1, and HQ2, workshops and conferences on the history of quantum theory sponsored by the Max Planck Institute for the History of Science in Berlin (June 2006 and July 2007) and the University of Utrecht (July 2008). The Max Planck Institute for the History of Science provided partial support to attend the two Berlin meetings. St. John’s University provided support for a sabbatical leave. Janine Lortz and the interlibrary loan staff of the Clemens and Alquin Libraries of the College of St. Benedict/St. John’s University were indefatigable in tracking down often obscure sources. The staff of the Niels Bohr Library (*AIP*) offered both assistance and hospitality during a 2005 research visit. For permission to quote from various published and unpublished materials, I am grateful to the American Institute of Physics (Dennison [1974]), the Bentley Library of the University of Michigan (repository and copyright holder for Dennison’s unpublished papers), The Bancroft Library of the University of California at Berkeley (repository for Birge’s unpublished papers), the Niels Bohr Library (*AIP*), College Park, MD (repository and copyright holder for some AHQP interviews), the Niels Bohr Archive, Copenhagen (repository and copyright holder for Bohr’s papers), the Museum Boerhaave, Leiden (repository for Ehrenfest’s papers), the Mathematics Institute, University of Göttingen [repository for Debye (1914) lectures], John David Jackson and the Physics Department of the University of California at Berkeley, Jean Kemble, Robert W. Birge, Peter P. Debye, Stanley Deser, Hans-Peter Hillig on behalf of the heirs of Max Planck, and Jun’ichi Hori. Joe Anderson (*AIP*), Marion Kazemi (*Archiv der Max-Planck-Gesellschaft*), Felicity Pors (*Niels Bohr Archive*), Robert W. Seidel (*University of Minnesota*), Anne J. Kox (*University of Amsterdam*) and Akiko Sugawara (*Hokkaido University*) all offered valuable advice for obtaining these permissions.

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