ROBERT D. PURRINGTON

# THE HEROIC AGE

*The Creation of Quantum Mechanics, 1925–1940*

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# ACKNOWLEDGMENTS

I learned my quantum mechanics from Bob Karplus, Mel Eisner, and John Gammel. Karplus introduced me to the subject with the help of David Bohm's classic book, Eisner's personal take on the subject allowed me to make it my own, and Gammel showed me how to apply it. Gammel, whose own contributions to two- and three-nucleon problems are well known, and who was a student of Bethe, completed my education in quantum mechanics and specifically the quantum theory of scattering, which occupied my attention for over a quarter-century after he guided my PhD research in the late 1960s. But from Mel Eisner I really *learned* quantum mechanics. He had the good sense to use as a text the book by Dicke and Witke, which emphasized fundamental ideas at the expense of applications. Although modest in appearance, that text influenced many successful physicists of my generation. Eisner's own idiosyncratic style, his willingness to challenge fuzzy thinking, his raised eyebrow when something less than cogent was uttered, showed a young graduate student how to think about theoretical physics. That Mel was an experimentalist highlights his particular gifts as a teacher.

Of course I learned more by teaching quantum theory for over four decades than I did by sitting in a classroom. In this I had the pedagogical guidance of the texts by Dirac, Schiff, Messiah, Merzbacher, and Sakurai. Other classics that have enriched my knowledge of the subject are those by Landau and Lifschitz, Kursunoglu, and Davydov.

On the other hand, when I commenced this project, I had only the barest knowledge of the history of quantum mechanics, and I suspect that most of what I "knew" was wrong. In this quest I have had no guide, which may lend this account a personal character. My interest in and knowledge of the history, historiography, and even philosophy of physics, is, however, long-standing. Those interests and skills date, in the first instance, to long discussions I had with the late Frank Durham, beginning over 30 years ago. Brief but influential encounters with the likes of Bernard Cohen, Joseph Agassi, Henry Stapp, Sam Westfall, Jed Buchwald, and Michael Hunter, to name just a few, have on the one hand taught me humility and on the other widened my intellectual horizons and suggested new avenues to explore.

In the end, however, this book arose as a logical intersection of my years of studying, teaching, and applying quantum theory, with my interest in history of physics. My book on 19th-century physics began as an exploration into the transition from classical to modern physics at the turn of the century, but I never escaped the 19th. That, in some sense, is a motivation for this study.

After reading the late John Wheeler's autobiography, in which he notes the influence of Baltimore's City College on his development, as well as the Enoch Pratt Free

Library, I am moved to do the same for City's rival Baltimore Polytechnic Institute, which had an important impact on me, despite my brief time there. As for Enoch Pratt, it would be hard to overstate the importance that the riches of the ground-floor reading room had on a teenager well over a half-century ago.

As always, access to primary and secondary sources in the history of quantum mechanics has been essential. Much of this has been made possible by Tulane University's Howard-Tilton Library with its extensive collection of important journals in German, its digital and Internet resources, and interlibrary loan. Some of these widely available resources include JSTOR and the Archive for the History of Quantum Physics. Nonetheless, and despite the availability of almost all journals on the internet, when those digital resources fail, as they sometimes do, it is valuable to have complete or near complete runs of important journals like *Nature, Philosophical Magazine, Proceedings of the Royal Society of London, Annalen der Physik,* and *Zeitschrift fur Physik*, just down the hall, as it were.

# PREFACE

As I write this, we have put the centenary of Bohr's theory of the hydrogen atom, perhaps the singular event in the history of quantum mechanics, behind us, and look forward to celebrating the 100th anniversary of the birth of quantum *theory* less than a decade hence. Several Bohr symposia spent 2013 trying to define precisely what Bohr's legacy is. His place in this narrative is somewhat odd and in a sense limited, because by the time the "new quantum theory" appeared in 1925, marking the starting point of our study of its literature and history, Bohr had virtually stopped contributing to the formalism of quantum mechanics, as opposed to its ontology.[1] At the same time, his authority had hardly waned, and in what follows few pages are totally devoid of his influence.

Quantum mechanics stands unchallenged as the great monument of 20th-century physics. Born at the very beginning of the century, it attained something like a definitive form by 1932, yet continued to evolve throughout the century, and its applications are fully a part of the modern world. Quantum computing, now so fashionable, may very well revolutionize contemporary life. In any case, although we live in a classical world, our lives are continually enriched on a daily basis by the applications of quantum theory.

It should come as no surprise that literature on the history of quantum theory is vast. Just one example of this is the monumental six- (or eight-) volume work by Jagdish Mehra and Helmut Rechenberg, *The Historical Development of Quantum Theory*,[2] written over two decades, and rivaled only by the 2000-page *Twentieth Century Physics* by Brown, Pais, and Pippard. Secondary works abound. But because the theory was essentially complete by the early 1930s, its basic history is actually manageable. The result is, that for the most part, the history of quantum mechanics has already been written, and many of the previous studies have benefited greatly from the fact that most of the founders survived into the 1950s and in a few cases, into the 1990s. One important consequence has been the oral history interviews of the Archive for the History of Quantum Physics project (AHQP),[3] consisting of first-person recollections of the early days of quantum theory. Of course the usual caveat applies here, that such recollections are often faulty, but it is probably fair to say that before quantum mechanics, no revolution in physics could have been documented and fleshed out from the oral histories of the major participants in the way that happened in this case. Although the journal literature continues to expand,[4] and many of these efforts will find their way into this narrative, for the most part my take on the events of 1925–1940 is based on my own reading of the primary sources.

So this is not a new story. It has been told in many places, superificially and exhaustively, successfully and otherwise. There are comprehensive, multivolume treatments like those of Mehra and Rechenberg, elegant, focused monographs such as that of John Hendry, idiosyncratic, episodic works along the lines of Beller, and so on. Abraham Pais's *Inward Bound* stands out as a wonderfully detailed and personal account of subatomic physics in the 20th century, but skips over most of the story told here. One might be tempted to write a better one-volume history of quantum physics than now exists, and I could be accused of trying to do just that, but my intent here is actually somewhat different. In short histories of ideas, the trade-off for brevity is often superficiality, a fate I have tried to avoid by showing in detail precisely where the important ideas on which quantum theory is based actually arose and usually where they first appeared in print. This information generally lies buried in papers by specialists focusing on narrow questions or in massive studies of the kind already mentioned. It will certainly not be found in the textbooks, and for the most part with good reason; the training of a physicist typically leaves very little time for contemplation and introspection. It is a cliché, but not less true because of that, that a major motivation for this work has been my inability to find a compact but comprehensive and detailed book on the subject.

Almost all of the sources used or cited in this work will be found at a good university library, and virtually all of the journal references are available online, even though access may not always be easy. The present work is only one way of looking at the subject, of course, focusing on the written record at the expense of correspondence among the principals that was so crucial to progress, the symposia and other meetings, and the hallway conversations that ensued. Although I have drawn heavily on these resources, to weave them into the narrative would simply have expanded it well beyond any reasonable size.[5] Quantum theory has a history that is important in its own right, and knowledge of that history not only enriches our understanding of the theory,[6] but an appreciation of how a particular idea or result came about may, and indeed should, offer important insights into how theoretical (or experimental) ideas emerge, and what their range of applicability or validity might be.[7]

Many of the papers relevant to this volume were originally published in German, of course,[8] frequently in *Annalen der Physik* or *Zeitschrift für Physik*, and only a small fraction of the important early papers have been translated into English.[9] This is largely a reflection of the fact that when they were published all physicists were expected to read, and even be able to lecture in, the German language. In some cases this has required me to personally translate papers into English, and where translations do exist I have relied on their accuracy. The assumption is that this will not introduce significant errors into this manuscript, but it remains at best an assumption. Frequently there will be no recourse but to cite the German original despite the lack of a translation. By the mid-1930s, as many Jewish scientists fled their homelands and as the *Physical Review* became increasingly important, supported by the continuing impact of British journals, the language of scientific discourse became English.

Without apology, this work takes as its starting point the current consensus and asks "how did we get here from there?" This is what historians (myself included) would call "whig" history, or "presentism;" even "triumphalist" history. That this is not the way history ordinarily ought to be written is obvious. It selects from the physics of the time only those discoveries that led to our present understanding, ignoring wrong turns or blind alleys. An analogy in the history of astronomy or cosmology would be to emphasize only Aristarchus's advocacy of the heliocentric theory and discard the geocentric theories of Aristotle, Hipparchos, Ptolemy, and everyone else. Nonetheless, and intentionally, few of the many blind alleys that necessarily were part of the development of quantum theory are pursued in this narrative. This turns out to be less of a defect than one might imagine, however, because the formalism of quantum mechanics matured so quickly, in not much over seven years, and was materially shaped by less than a few dozen physicists, so that there is a much thinner record of wrong turns and controversies than there might otherwise be. Finally, and although scientists–historians and historians of science often do not agree on this point, it is fair to argue that because science does inexorably progress, though not without setbacks and periodic rethinking and retrenching, it does move forward, and I make use of that fact without apology.

Yet we all know that published work, that is, journal papers or review articles, fail to fully capture the history of an idea or discovery; we can look to our own work for that insight. The final paper is the polished end product of a typically complex, halting, and messy process that is typically moved forward by hunches and speculations that often as not are totally missing from the published papers. The road to a discovery might be quite formal and logical, but more frequently it will be almost devoid of these characteristics. Much of the evolution of a theory or understanding of an experiment will have taken place in correspondence, at conferences, over coffee or tea, in a bar, on a climb or a ski slope. Today it might be technology: email, the Internet. But for a discovery to become "official" or canonical, and thus enter the secondary literature and become part of everyday practice, it will have had to meet the test of "peer review," or at least receive an editor's stamp of approval, and come into print.[10] The peer-review process that we alternately deride and praise today was not nearly as well developed in the 1920s, but it is nonetheless true that what may have been discovered in a mountain cabin in Austria or in an office in Göttingen had to reach print before its import and validity could be judged and before it could become influential. Once on the page an idea becomes part of the literature, to be incorporated into textbooks for the next generation, or perhaps even to be shown wrong.

With the notable exception of the introductory chapters, which serve to bring the reader up to date on the situation before the new quantum mechanics appears in 1925–1926, this work concentrates on the decade-and-a half ending in 1940. If the choice of this period seems arbitrary, I think it is not. One could argue that the period between the wars is the natural period to treat, and in a sense I have done that by devoting considerable space to setting the stage for 1925. And terminating this narrative in 1940 (or 1939 or 1941) is appropriate for two reasons. In the first place, the hiatus caused by the war represents something of a period of gestation, so that quantum physics was very different in 1947 from that in 1939, in part because of the fruits of war-related research. But this hiatus meant that relatively little of importance was published between 1939 and 1947. In the end, however, it is simply a matter of manageability. Prior to WWII, the community of quantum scientists was small, but grew rapidly after the conflict, with enormous resources spent on rebuilding the affected nations, and with the rise of large-scale funding of science by governments, fueled in part by the Cold War. The literature began to grow rapidly, making it impossible to try to continue to survey it and still retain some scale. The reader will notice a certain lack of discipline in this regard, however, so that in a few cases, nuclear physics and astrophysics in particular, it seemed appropriate to follow the trail of writing on a subject to its denouement as late as 1948–1949. Perhaps the most egregious example of ignoring our self-imposed constraints comes in the discussion of the interpretation of quantum mechanics. But because this issue hangs like a cloud over the theory, I have felt obligated to give some flavor of developments in the last four decades, as issues that for the most part arose in the 1920s and 1930s have not only been elaborated, but actually subjected to experimental tests. As an aside, it is worth noting that the period on which we concentrate here is essentially the same as that covered in Mehra and Rechenberg's vol. 6 (1926–1941), in well over 1000 pages.

As will become apparent, the formalism of quantum theory was substantially in hand by 1932, so that one might ask, why 1940? It turns out that many important implications of the theory were discovered in those prewar years, especially in the application of quantum mechanics to atoms, nuclei, and solids. Without some acknowledgment of these developments, the story would be incomplete.

It may seem strange that the interpretation of quantum theory is still very much an open question. Yet in the 80 years since von Neumann first wrote about the paradoxes inherent in the quantum theory of measurement, there has never been a hint that disagreements about interpretation have any bearing on the explanatory power of the theory. This remarkable situation is perhaps without parallel in the history of science, but, in any case, because much of the writing on the interpretation of quantum mechanics is fairly recent, if the last half-century can be seen as "recent," we will only be able to scratch the surface, so to speak. Although these open issues of interpretation are very unlikely to threaten its validity as a program for calculating the results of experiments, they touch on, in very profound ways, the *meaning* of quantum mechanics. I provide some guide to this literature, but because it is very much an open topic, I cannot linger too long over its details. How the reader decides to deal with these issues—if at all—is a matter of taste or strategy.

Although the theory had matured well before the outbreak of WWII, so that most of the material discussed in a modern textbook from the 1980s or 1990s will have been developed in those prewar years, a few recent topics of special relevance that would not be found in books written in the immediate postwar era (or would have been given short shrift) are also touched on here, if briefly, when coherence or completeness seems to require it. I do not try to cover the literature of quantum-field theory or even quantum electrodynamics in detail, but again, I do not avoid it altogether. Relativistic quantum theory is almost as old as quantum theory itself, with Schrödinger trying a relativistic theory before his nonrelativistic wave mechanics. Dirac developed the relativistic theory of the electron ("Dirac equation") as early as 1928, and for all practical purposes founded quantum electrodynamics in those same years. But the great successes of quantum electrodynamics and quantum-field theory are mostly postwar.

There are, of course, many unanswered or open questions that qualify any consensus view of how quantum mechanics evolved, some of which originate in newly discovered biographical details of one or another of the founders, occasionally in some newly discovered correspondence. Most of the open issues, however, concern not the history of quantum mechanics, or its formalism, but rather its meaning and interpretation, in the form of questions that still haunt the theory the better part of a century after its creation. The caveat that might be added is one that arises in thinking about how to reconcile quantum theory and the theory of gravity, which for the moment is general relativity. There is no way to know the direction this exploration will take, but it could have a fundamental impact on how quantum theory is formulated. But that is for the next generation.

With the exception of those observations that fostered the quantum revolution, and especially atomic line spectra, I touch on experimental results only when they are essential to the narrative, and then only briefly. To some degree that decision is merely a matter of economy, and it certainly does not represent a judgment on the relative value of theory and experiment in this story. Indeed experimental results played an unusually direct role in the origins of quantum mechanics. But quantum *theory* is a theoretical construct, and for that reason the story has to be about how the theory evolved, however much that may have been driven by experiment.

There is naturally interest in what might be called the sociology of quantum mechanics, the cultural and philosophical milieu in which the theory was born and how that context affected the creation and even the nature of quantum theory. It is interesting, however, that Max Jammer, who wrote what is perhaps the definitive work on the philosophy of quantum mechanics, found little reason to address the question of how European philosophical movements, especially positivism, could be seen as laying the groundwork for the discoveries of Einstein, Bohr, Heisenberg, Schrödinger, Dirac, Pauli, and others. Nonetheless, we are not so naive as to believe that quantum mechanics was not influenced by its time and place in history.

Although this is not the place to survey the textbook literature on quantum mechanics in detail, there is arguably no other literature that shows so directly the evolution of the field; those ideas that have proven to be especially efficacious in advancing the understanding quantum systems quickly find their way there. There are many excellent texts on quantum mechanics for those who want to learn the theory and even some popular introductions that try to give some flavor of it.[11] Indeed there may not be another area of physics that has spawned so many excellent texts. A few even treat the history of the subject with skill and subtlety. And yet times change, fads, or at least emphases, come and go, even in the textbooks. The situation is complicated by the fact that not too much over a decade after the initial papers on the new quantum mechanics appeared, the world was plunged into war again. This means two things: First, that some discoveries in quantum mechanics and its progeny, nuclear physics, were not published in the open literature until well after the conclusion of the WWII,[12] and second, that for nearly a decade physicists were either occupied with war-related research or were in areas where research and publication was impossible, from at least 1939 until 1945, or even later. If we add to that German anti-Semitism of the 1930s and the disruption in careers that resulted, we can see that the record, in both the primary and secondary literature, is spotty, with at least a semi-hiatus of over a decade. Thus the textbook literature is less revealing than might be otherwise.[13] It is also true that after the new quantum mechanics reached a kind of maturity in the early 1930s, much of the subsequent effort was in applications to molecules, nuclei, and solids. I provide a guide to this literature of applied quantum mechanics.

We should not forget that the physicists who created quantum mechanics in 1925–1932, with a small number of exceptions, were all from the generation that was born in the first decade of the 20th century: Pauli, Heisenberg, Jordan, Dirac, von Neumann, Bethe, and Gamow were all born between 1900 and 1906. Only Einstein, Born, Bohr, and, most surprisingly, Schrödinger, were of the previous generation.

The reader will not find many equations in this book, and only a few detailed developments or discussions of a particular discovery or proof of some result. To have elaborated in this way would have defeated my purpose and would have expanded this work beyond reasonable and practical bounds. The original sources are laboriously cited, as are, in many cases, secondary works that provide explication and context. The reader can pursue these developments at his or her leisure. The alternative would be a book many times the size of this one, and essentially a full-blown text on quantum mechanics, with historical asides. The principal exception to this is a brief discussion of Heisenberg's revolutionary paper that in many ways began the quantum revolution, in the Appendix.

A bibliographic essay had to be sacrificed to my prolixity in other areas, and it ought to be mentioned that the references to each chapter do not fully reflect the sources that went into the narrative; as is always the case, I have had to be judicious in the sources I have cited. Assume if you will, however, that your missing source has probably found its way into this work in some fashion.

## NOTES

1. Although his career in the technical sense underwent a resurgence in the late 1930s with his compound nucleus model. See Chapter 15.
2. Indeed, Mehra was able to interview most of the founders of quantum theory. It has to be said that there are serious organizational problems in Mehra and Rechenberg (1982–2000) that do not, however, negate much of the evidence presented there. In fact, vol. 6, which is a sort of summation of what has come before, can profitably be read on its own. Its historical focus is almost precisely that of the present work, but its scope is quite different.
3. To which the *Sources for History of Quantum Physics* project provides a guide and overview The archives are monumental and indispensable. The way in which they can enrich the history of quantum theory can be seen in a work like John Hendry's gem, *The Creation of Quantum Mechanics and the Bohr-Pauil Dialogue* (Hendry, 1984).
4. Notably in *Historical Studies in the Physical Sciences* and *Archive for the History of Exact Sciences*.

5. For those whose interest is more in the personalities of the founders of quantum mechanics than in the theory, there is the somewhat glib and gossipy *The Quantum Ten* by Sheila Jones. Although not flawless, the history is sound enough to deserve a seriously qualified recommendation, and the same caveat applies to the science, which is a bit surprising from someone with a background in theoretical physics.
6. The point has been made that the history of a discipline, say, is the equivalent of an individual's personal memory. Without those memories, who are we?
7. Eric Scerri has expressed a somewhat different view: " . . . many argue . . . that it is actually a hindrance for the practitioner to get too involved in the historical aspects of the theory." It seems to me that there is little danger of that. See, for example, Elkana (1977).
8. And a few in French or Italian.
9. Some important contributions should, however, be mentioned. Pergamon's *Selected Readings in Physics* series published several volumes of papers that included many previously untranslated. Of special relevance here are *Nuclear Forces* by Brink (1965), *The Old Quantum Theory* by Ter Haar (1967), and *Wave Mechanics* by Ludwig (1968). Van der Waerden's indispensable *Sources of Quantum Mechanics* (1967) does much more than merely translate early works in matrix mechanics. His participation in these events has given him the perspective to provide much additional context.
10. This has been changed to some extent by the existence of the e-print archive arXiv.org and other forms of rapid, often barely reviewed, publications, but this is product of the digital era entirely. Preprints, of course, have been a major form of scientific communication for decades, but only rarely—if ever—will such a medium intrude into our discussions.
11. Notably the just-published *The Quantum Moment* by Crease and Goldberger (2014).
12. There was a similar lacuna during WWI, but quantum theory was in its infancy then.
13. In fact, a comparison between even the best and most up-to-date of the texts from the late 1930s, such as Rojansky, and those that appeared 3–4 years after the end of the war is very revealing and deserves further study.

PART I

# Forbears

# 1

## "CLOUDS ON THE HORIZON"
## NINETEENTH-CENTURY ORIGINS AND THE BIRTH OF THE *OLD QUANTUM THEORY*

### INTRODUCTION: *FIN DE SIÈCLE*

By the middle of the 19th century physics was evolving toward a form that most physicists would recognize today. The major figures in this consolidation of classical physics were James Clerk Maxwell, Lord Kelvin (William Thomson), G. G. Stokes, and a few others in Britain, along with Rudolf Clausius, Hermann Helmholtz, Gustav Kirchoff, and Ludwig Boltzmann in Austria and Germany.[1] Much of this work was built upon mathematical foundations laid down by Kelvin George Green, and their 18th-century predecessors (Augustin-Louis Cauchy, Leonhard Euler, etc.). Most of them were what we would think of today as theoretical physicists, though Maxwell, Kirchoff, and Helmholtz were quite at home in the laboratory. Although many will argue that today's strong separation between experimental and theoretical physics (or physicists) began in the 20th century, the trend was well under way before Maxwell's death in 1879.

At the same time that the science of thermodynamics, centering on its first and second laws, was being developed by Kelvin and Clausius, electromagnetic theory was being formulated by Kelvin, Maxwell, and Helmholtz, founded upon the experiments of Michael Faraday, André-Marie Ampère, and others. Even classical mechanics, which was largely an 18th-century science elaborated by Pierre-Simon Laplace, Joseph-Louis Lagrange, Euler, Pierre Louis Maupertuis, and others, saw important advances in the 19th century, including celestial mechanics, especially the three-body problem, the work of Carl Jacobi and W.R. Hamilton,[2] and eventually the work of Henri Poincaré at the century's end. Continuum mechanics, in the form of fluid dynamics and elasticity, lagged behind a bit, but was being advanced by Kelvin, Stokes, Claude-Louis Navier, and others.[3] Thus, by the end of the 19th century such a towering figure as Kelvin could see physics as essentially complete.[4] The first American Nobel Laureate Albert Michelson wrote that "the more important fundamental laws and facts of physical science have all been discovered."[5] This turned out to be a monumental error, as we all know,[6] and indeed there were "dark clouds" on the horizon, as Kelvin noted,[7] as early as the 1870s, that would force a complete rethinking of mechanics and electromagnetic theory and ultimately lead to the quantum revolution.[8]

It is a crucial point that although that other great revolution of the 20th century, the theory of relativity, had very little in the way of an empirical foundation, depending on how one incorporates the efforts of Michelson and Morley into the story, quantum theory, by contrast, was built almost entirely upon a foundation of experimental results and observations that had been accumulating since just after 1850.[9] Together, these two theories, which so exemplify 20th-century physics, provide illuminating case studies in the nature of scientific progress and discovery through the sharp contrast between the ways each evolved. Some of this is due, of course, to the unique personal style of one man, Albert Einstein. The larger story, of the transition from classical to quantum physics, has been told in several places,[10] and for that reason only the briefest recounting is given here.

## TRANSITION

Because a defining characteristic of the history of quantum mechanics is that it was so thoroughly experiment driven, we will take some time to examine the most important of the challenging and unsolved problems that loomed over theoretical physics as a result of experiments carried out in the last few decades of the nineteenth century.[11] It hardly needs to be added that there was little appreciation at the time of the impact these experiments would have in ushering in the revolution that was about to take place. This situation is not unusual; historically it is rare to find a situation in which there exists a clear sense that a series of perplexing experimental results or observations would require a total break with the past,[12] a paradigm shift if you like. In most cases the recognition comes long after it has happened, and a case in point is that of Arnold Sommerfeld, perhaps as representative of the transition as anyone, and certainly an important participant in it, who in 1929 thought that the new quantum theory, then 4 years old, "did not signify a radical change."[13]

One caution is in order as I emphasize the empirical roots of the quantum revolution, which is—and it does not take much sophistication in the philosophical underpinnings of science to understand this—that rarely is experiment unguided by theory, even theory that will eventually be abandoned, and even in the case of someone like Michael Faraday, seemingly the quintessentially naive experimenter. There are, however, episodes in the history of physics when existing theory is able to shed very little, if any, light on emerging experimental results, and it can be argued that this was one of those.

## SPECIFIC HEATS

The kinetic theory of gases of Maxwell, Clausius, and Boltzmann,[14] and in particular the *equipartition theorem*, provided an explanation of how energy was apportioned among translational degrees of freedom of a monatomic gas and the additional vibrational and rotational degrees of freedom of a diatomic or triatomic molecule. Up to a point, the observed specific heats could be understood in terms of the still-young and somewhat controversial atomic theory, and, indeed, provided strong support for it. It was known from the observed specific heats of monatomic gases and others at low temperatures, along with kinetic theory, that each degree of freedom contributed $1/2kT$ of energy per atom or molecule, where $k$ is Boltzmann's constant. In the case of a monatomic gas, with only 3 degrees of freedom, the specific heat at constant volume, $c_v$, should be $3/2k$.[15] At constant pressure, some of the heat goes into expanding the gas (doing work), so that $c_p$, the specific heat at constant pressure, should be $(3/2k+k)=5/2k$. The ratio $\gamma = c_p / c_v$, which is independent of $k$ (or $R$), i.e., a dimensionless quantity, should then be $5/3$. As early as 1857 Clausius was assuming that a diatomic molecule such as $H_2$ had 6 degrees of freedom (three translational, three rotational), and that $\gamma$ should equal $4/3$.[16] Experimentally, however, it was found that $\gamma$ was approximately 1.4. In 1860 Maxwell saw this as a great crisis, writing that this "overturns the hypothesis [of equipartition], however satisfactory the other results may be."[17] In 1875, 4 years before his death at the age of 48 from stomach cancer, he observed of this problem that "here we are brought face to face with the greatest difficulty that the molecular theory has encountered."[18] The measured value of 1.41 could be obtained only by assuming that 1 degree of freedom did not contribute to the energy (for then $c_v = 5/2$ and $c_p = 7/2$; $\gamma = 7/5 = 1.4$). It was only in 1877 that Boltzmann made the proposal that rotation about the symmetry axis did not contribute to the energy, yielding the theoretical value $\gamma = 7/5$, very close to experiment. It had also been found that $\gamma$ for mercury vapor was about 1.67, exactly what would be expected from translational degrees of freedom alone.

Note that when Maxwell made his comment, vibrational degrees of freedom were not being taken into account, and they would have raised $c_v$ to $7/2k$, lowering $\gamma$ to $9/7 = 1.29$ (or 1.25 depending on the number of rotational degrees of freedom). Thus the situation was much worse than Maxwell thought, and in 1900 Lord Rayleigh (John William Strutt) noted that "the law of equal partition disregards potential energy," and went on to say that "what would appear to be wanted is some escape from the destructive simplicity of the general conclusion."[19] Soon the specific heats of molecular hydrogen were measured over an increasingly large range of temperatures, especially higher temperatures, and the behavior turned out to be very puzzling (Figure 1.1).

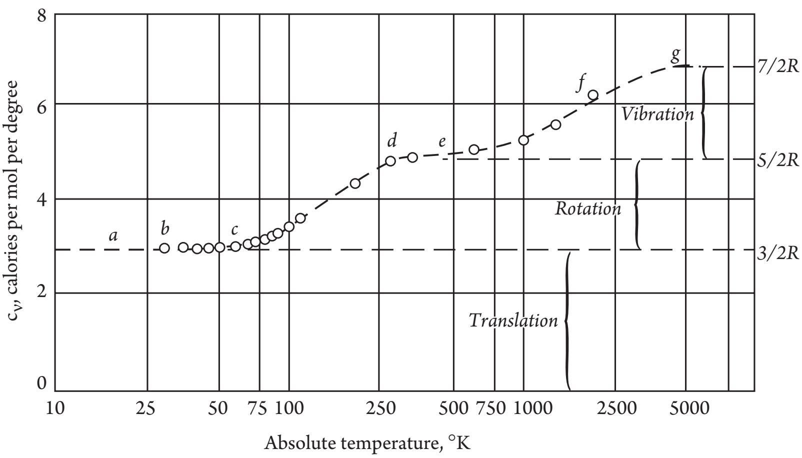


**Figure 1.1.** Specific heat of a typical gas as a function of temperature, showing excitation of rotational and vibrational degrees of freedom. Richtmyer and Kennard (1942), by permission of McGraw-Hill.

$c_v$ was found to be approximately $5/2k$ at room temperatures $(\gamma = 7/5)$, matching the "dumbbell model" with 2 rotational degrees of freedom, but was strongly temperature dependent, being approximately $3/2k$ below 60 K $(\gamma = 5/3)$ and $7/2k(\gamma = 9/7)$ at very high temperatures. Clearly only translational degrees of freedom were excited at low temperatures; rotations began to be excited at around 100 K, and finally 2 additional degrees of freedom, evidently due to vibrations, were excited beginning near 500 K.[20] Instead of the rotational and vibrational degrees of freedom contributing to the energy and hence the specific heats at all temperatures, there were abrupt transitions from one value of the specific heat to another, as can be seen Figure 1.1. This was, indeed, one of the very first pieces of evidence that what we would call quantum phenomena existed, that as was later discovered, rotational or vibrational degrees of freedom were not excited until there were sufficient energy quanta available to cause the system to make a transition to a higher state. No explanation would be possible before the advent of quantum theory.[21]

A similar problem arose with the specific heats of solids and the law of Pierre Louis Dulong and Alexis Thérèse Petit that predicted the value $3k$ (or $3R$), contrary to what was observed at low temperatures.[22] As we shall see, Einstein's attack on this problem in 1907[23] was one of the decisive events in the unfolding evolution of the quantum theory, and one that is not widely appreciated. It was, as Martin Klein has emphasized,[24] the very first application of quantum theory to matter as opposed to radiation. Out of the latter had come Max Planck's 1900 paper and Einstein's analysis of the photoelectric effect, in 1905, introducing the energy quantum into radiation theory. But Einstein's treatment of the problem of specific heats of solids made clear, first, of course, to Einstein, and then to his audience, that the nascent quantum theory had to apply *everywhere*. This was truly revolutionary. I discuss the problem at greater length in Chapter 18.

## BLACKBODY RADIATION

The problem of the spectrum of "cavity" or "blackbody" radiation dates back to the late 1850s and the early measurements of Kirchoff and others. Attempts using the thermodynamics and kinetic theory of the 1860s, that is, equipartition, the Maxwell–Boltzmann distribution, or Boltzmann's early statistical mechanics of the 1880s, were only partially successful, and, as is well known, suffered from an "ultraviolet catastrophe"[25] (Figure 1.2). This conundrum motivated Planck's search for the correct functional form of the blackbody spectrum and his "successful" attempts to justify it from statistical mechanics. Unlike the problem of atomic spectra, this one did not scream discontinuity at the outset. Whether Planck had a clear idea of what he had done is a matter for debate, but, in the sense of historical influence, there is no doubt that, right or wrong, it is in Planck's 1900 paper that the quantum was born.[26] His introduction of the new constant, $h$, with units of angular momentum,

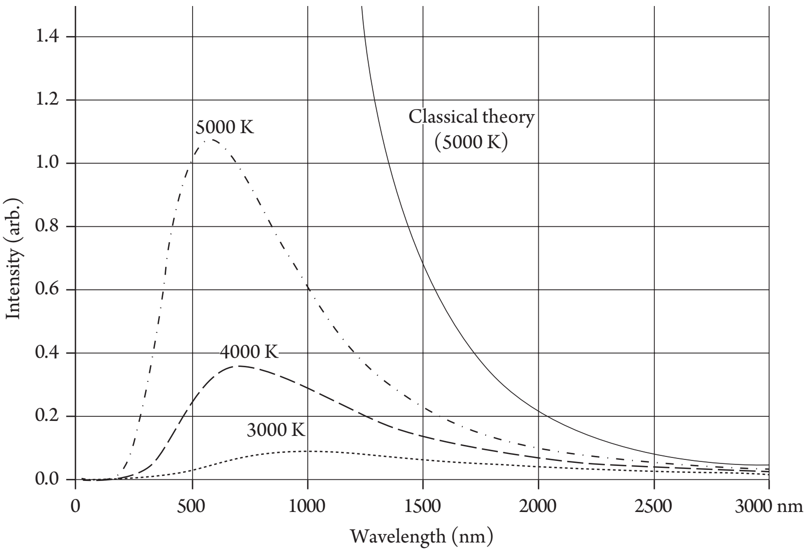


**Figure 1.2.** "Ultraviolet catastrophe," showing divergence of the classical Rayleigh-Jeans law at short wavelengths. Enge et al. (1972), by permission of Addison-Wesley.

meant that a fundamental unit of length could be derived from the electron charge $e$, its mass $m$, and $h$. That length, $h^2/me^2$, has the value $2 \times 10^{-7}$ cm, a characteristic atomic size.[27]

## PHOTOELECTRIC EFFECT

The photoelectric effect, in which electrons are ejected from a metal surface because of an incident electromagnetic wave, was first observed by Heinrich Hertz in 1887,[28] and it became known as the Hertz effect. The first serious studies of it were by J. J. Thomson in 1899, using ultraviolet light, and by Philipp Lenard, who in 1900–1902, showed that the effect defied explanation in classical terms.[29] Together they found that no matter what the intensity of electromagnetic radiation incident upon a metal surface, electrons were not ejected until the energy (frequency) was sufficiently high. Not long after, in his 1905 paper "On a Heuristic Point of View About the Creation and Conversion of Light,"[30] Einstein introduced the novel idea of the quantum of light to explain the effect.[31] In that paper and one the next year he essentially reinterpreted Planck's introduction of quanta in the 1900 paper, which was really only implicit, and, it can be argued, created the quantum concept then and there. His 1916–1917 papers on the emission (spontaneous and stimulated) and absorption of radiation further solidified the concept of the quantum of electromagnetic energy, carrying linear momentum $h\nu/c$.[32] The scattering of x-rays by electrons in the "Compton effect," discovered by the

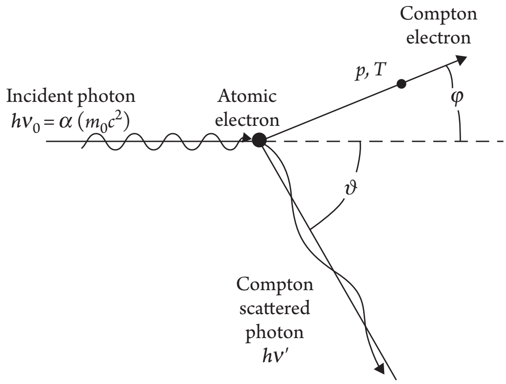


**Figure 1.3.** Compton scattering. From Evans (1955), by permission of McGraw-Hill.

American physicist Arthur Holly Compton in 1922–1923, convincingly demonstrated the importance of a particle-like description of electromagnetic radiation (Figure 1.3).

## WAVE–PARTICLE DUALITY

The mysterious property of matter, *wave–particle duality*, was first mooted by Einstein in 1905, when in interpreting the photoelectric effect, he proposed what came to be known as the *photon*, the light quantum. Interference and diffraction phenomena had long made it clear that electromagnetic radiation consisted of wave motion,[33] but Einstein's analysis of the photoelectric effect, his decisive paper on the emission and absorption of radiation, and finally, the Compton effect,[34] showed that light exhibited discrete, particle-like properties as well. Eventually the understanding came to be that light is "something else," neither wave nor particle, but exhibits one or the other property depending on how it is observed.

Another decade would pass before symmetry would be restored to the wave–particle question. This happened in 1923–1924, when Louis de Broglie (Louis-Victor-Pierre-Raymond, seventh duc de Broglie) suggested that a particle of momentum $p$ possessed (in some sense) a wavelength of $\lambda = h / p$. This daring proposal, that particles also ought to possess *wave* properties,[35] was at the time not much more than a conjecture, with essentially no experimental support, but soon the electron-diffraction experiments of Clinton Davisson, Charles Henry Kunsman, and Lester Germer at Bell Labs, as well as those of G. P. Thomson and Andrew Reid in Cambridge, beginning as early as 1923, but culminating in 1927,[36] made the conclusion that particles can exhibit wave properties that are almost inescapable (Figure 1.4). Eventually, the quantum-theoretical understanding of the Ramsauer–Townsend effect[37] buttressed this understanding.

Electron diffraction had already been predicted by Walter Elsasser after he read de Broglie's thesis.[38] He suggested that an experiment should be attempted to test the hypothesis, but supposedly the experimentalist James Franck, with whom the 21-year-old Elsasser was trying to work at Göttingen, replied that such an experiment was unnecessary because the phenomenon had already been observed in Davisson's

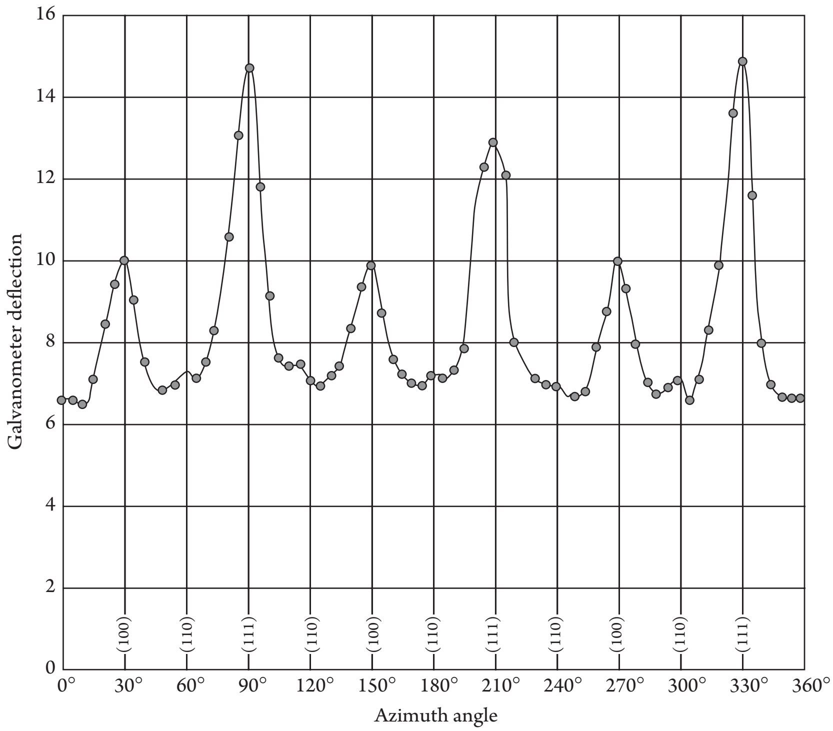


**Figure 1.4.** Electron diffraction experiment of Davisson and Germer. Intensity of electron scattering vs. azimuthal angle. Davisson and Germer (1927b), by permission of American Physical Society.

experiments.[39] By the time of this verification, Erwin Schrödinger had constructed his wave mechanics, drawing its inspiration from de Broglie's hypothesis and lending some plausibility to it.

## ATOMIC SPECTRA

The existence of discrete emission lines in the spectra of excited atoms and the similar phenomena of discrete absorption spectra, including that of the sun (first noticed in 1802), posed a problem similar to that of specific heats, and one that arose much earlier.[40] Indeed, much of the effort in experimental physics in the late 19th century and the first two decades of the 20th was devoted to atomic and molecular spectra. It was suggested that the discrete lines represented periodic molecular vibrations, that is, classical normal modes, but it would have been very difficult to explain the discrete emission or absorption spectrum of monatomic hydrogen on this basis. Hydrogen, of course, was the canonical case, with its very familiar "Balmer series" (1885) of spectral lines in the visible spectrum. Investigations outside the visible spectrum led to the fundamental discoveries of Johannes Rydberg and Walter Ritz, and in particular the *Ritz combination principle* of 1908.[41] What was not yet understood was that the emission or absorption lines represented energy *differences* between discrete states. But in 1913–1914, just as Niels Bohr was proposing his theory of hydrogen, Franck and Hertz found that electrons passing through mercury vapor were absorbed only if their energy reached 4.9 eV.[42] Soon Bohr showed that this could be interpreted as the discrete ionizing energy of mercury,[43] further establishing the existence of discrete levels, and characteristic x-ray spectra raised similar problems. The Bohr theory of the hydrogen atom would provide a convincing explanation of the discrete lines, and, of course, the details of the Balmer series. We explore these issues in detail in future chapters.

## X-RAYS, RADIOACTIVITY, AND THE NUCLEAR ATOM

Although radioactivity, as a mostly nuclear phenomenon, did not immediately demand a quantum explanation, it seemed to be beyond the explanatory power of classical physics as understood in the years around 1900. For quite some time, studies of radioactivity were in a primitive, taxonomic stage, in which it was not even clear what the phenomena were. The discovery of x-rays by William Röntgen in 1895[44] raised a whole host of questions, including whether they were a form of electromagnetic radiation. And the discovery of characteristic x-rays by Henry Moseley[45] posed problems similar to those arising from discrete optical atomic spectra.

Henri Becquerel's[46] accidental discovery of radioactivity in 1896 complemented that of Röntgen in the previous year, and this was followed by Ernest Rutherford's discovery of $\alpha$- and $\beta$-rays emitted in the decay of uranium and thorium sources in 1899. In 1903 he called the third kind of radiation from radium, discovered by Paul Ulrich Villard in 1900, $\gamma$-radiation. In only 8 years around the turn of the century, virtually all of the basic phenomena of radioactivity had been discovered. Soon after the discovery of $\alpha$-rays, the $\alpha$-scattering experiments of Rutherford and his colleagues[47] revealed the nuclear atom and hinted at the existence of new forces and hence entirely new physics, but again, the quantum nature of the problem became apparent only later. We discuss these experiments of Rutherford and his collaborators in detail in Chapter 15, but the nuclear atom, with its orbiting electrons, immediately raised the question of atomic stability, because in Maxwell's theory accelerated electrons would radiate energy and spiral into the nucleus. This problem, as it turned out, could be dealt with only quantum mechanically. Bohr's model of hydrogen, although a historical watershed, provided only a partial and tentative solution.

All of the issues associated with radioactive decay, including the nature of $\alpha$-particle emission and $\beta$-decay, the identification of the parent and daughter nuclei, the quantization of electronic charge,[48] the radioactive inert gas radon, etc., were being enthusiastically studied by Marie and Pierre Curie, Rutherford, and others in the years leading up to the war, just as Bohr was about to publish his first paper on hydrogen.[49] Alpha-decay would turn out to be a fundamentally quantum phenomenon, involving quantum tunneling, a discovery made by George Gamow in 1928,[50] but only after quantum theory had been created. From these studies of radioactive decay, and later scattering experiments carried out in Rutherford's laboratory, would eventually emerge the realization that there were two new forces of nature, the strong and weak nuclear forces.

## ON THE THRESHOLD

Initially it was the Planck–Einstein idea of quanta of vibrational or electromagnetic energy that solved the problem of blackbody radiation, and, as we have seen, it was also in a paper of Einstein's that the riddle of the photoelectric effect was explained by invoking the quantum of electromagnetic energy. Although the general acceptance of the idea of the particle aspects of light may have had to wait for Compton's experiments, Einstein's Nobel Prize in 1921 reflected a growing acknowledgment of it.[51] The name *photon* was coined by G. N. Lewis 3 years after Compton's work.[52] And, as we have noted, the deployment by Einstein in 1907of these quantum ideas in attacking the problem of the specific heat of solids was the first application of the quantum to something other than radiation.

A decisive event in the history of the quantum theory was the first Solvay Conference in Brussels at the end of October 1911, involving Hendrik Lorentz, Planck, Einstein, Walther Nernst, and over a dozen other prominent figures, including the great turn-of-the-century mathematical physicist Jules-Henri Poincaré.[53] Much of the discussion at the conference centered on the meaning of the "quantum of action," *h*. At that point, special relativity had been embraced by most far-seeing physicists, and now the issue was the seeming fact of quantum discontinuities, exhibited in the empirical evidence we have just discussed, as well as in the theories of Planck and Einstein. Poincaré is an especially interesting case because he came to the conference pretty much ignorant of quantum theory, but within a month had written a major paper for *Journal de physique* on the subject.[54] In a real sense Poincaré epitomizes the transition that was just beginning. Among important ideas offered at the conference was the opinion that quantum discreteness seemed to imply that physics could no longer be described by differential equations.[55] This conundrum would be central to the controversies of 1925–1926, as matrix mechanics with its built-in discontinuities, and wave mechanics, framed in terms of differential equations, emerged and vied for supremacy.

## THE OLD QUANTUM THEORY; THE BOHR THEORY AND ITS AFTERMATH

The term old quantum theory is traditionally restricted to the theory prior to de Broglie's hypothesis of 1923–1924, or perhaps Heisenberg's first paper 2 years later. It represents the attempt, largely within the classical paradigm, but nonetheless incorporating the idea of the quantum, to explain the troublesome experimental results I have enumerated. An excellent short summary of the old quantum theory, and especially the growing realization of the defects of the theory in 1924–1925, can be found in chapter 1 of Condon and Morse's book of 1929.[56] As late as 1925 Max Born, who would be directly involved in breaking the impasse, wrote in his "Lectures on Atomic Mechanics" that "At present we have but a few vague indications about the kind of deviations from classical laws that must be introduced for the explanation of atomic properties . . . therefore perhaps the second volume [of this work] so-planned will remain for many years unwritten."[57] In fact it would only be a few months before the long-sought explanation would begin to emerge, and Born would be one of its parents.

The first and greatest triumph of the old quantum theory was Bohr's treatment of the hydrogen atom in three papers in the *Philosophical Magazine* in 1913, known colloquially as "The Trilogy."[58] But the place of the Bohr theory of hydrogen in the history of quantum mechanics is so central that a detailed discussion of it is left for the next chapter. Of course, Bohr's theory of hydrogen would have been impossible had it not been for Rutherford's discovery of the atomic nucleus only 2 years earlier and in the laboratory where Bohr would soon be working.

During the decade following Bohr's theory of hydrogen, the old quantum theory was elaborated with some qualitative successes, but in a patchwork manner and without anything that could be called a fundamental theoretical framework,[59] in spite of tireless efforts by Bohr, based on his correspondence principle, and by Arnold Sommerfeld and others.[60] Sommerfeld generalized the Bohr quantization condition (see Chapter 3) to the "action integral" $\int p_i \, \mathrm{d}p_i = n_i h$, where $p$ and $q$ are canonically conjugate momentum and coordinate variables (there is also a related *angle* variable) and $n$ is an integer.[61] This came to be known as "the quantum principle" or "quantum condition." This formulation, which attempted to bridge the gap between classical and quantum theory, gave good results in simple systems, but had already failed when applied to the neutral helium atom, for example.[62] As Condon and Morse wrote in 1929, "Even when it gave correct results . . . there was an unsatisfactory looseness about the principles. The quantum conditions were added to ordinary mechanics as an afterthought, so to speak, instead of being an integral part of it."[63] As with much of the formalism that seemed promising in the post– WWI era, this rule foundered when more widely applied. More generally, wrote Bohr in 1925, ". . . one is faced not with a modification of the mechanical and electrodynamical theories describable in terms of the usual physical concepts, but with an essential failure of the pictures in space and time on which the description of natural phenomena has hitherto been based."[64]

The almost Olympian figure of Bohr dominated attempts to arrive at a description of quantum phenomena in this period of interregnum, so to speak, the decade between the Bohr theory of hydrogen and and de Broglie's thesis. Bohr's was the most respected voice, and after 1921 his institute in Copenhagen was a mecca for those attempting to solve the problems that nature was presenting.[65] His survey papers of 1916 and 1922[66] in many respects pointed the way for those who would take the torch from his hands and carry it forward, especially Werner Heisenberg, Pascual Jordan, and Wolfgang Pauli. If Bohr's writing failed to offer anything like a solution, it made clear where the problems lay.

More than any other single idea of the time, Bohr's *correspondence principle* guided attempts to create a quantum theory of atoms in the 1920s. Its assertion that any valid quantum theory must merge with the corresponding classical theory in the limit of large quantum numbers could be taken as merely an expression of the fact that quantum mechanics is *the* theory of matter; that it applies for both large and small quantum numbers, and therefore a quantum description must merge into the classical one at some point. One statement of this principle by Bohr goes as follows: "we may expect that any theory capable of describing [these phenomena] in accordance with observation will form some sort of natural generalization of the ordinary theory of radiation."[67] If it is rarely spoken of today, its implications are nonetheless universally accepted. It is demonstrable that specific theoretical developments of the 1920s were directly motivated by the correspondence principle. Of this I will have more to say.

From the perspective of the early 21st century, it is undeniable that the most important developments in atomic physics in the first two decades of the previous century were experimental, not theoretical. Theoretical breakthroughs that took place between 1913 and 1923 were for the most part illusory, or at the very least, ad hoc. There are exceptions, however. For example, Sommerfeld and his student Pieter Debye discovered space quantization in 1916 in the process of providing an explanation of the Zeeman effect.[68] This discovery, that the projection of the angular momentum vector on a chosen axis was quantized, was a major discovery, one that provided further confirmation of the discrete character of the microscopic world, and in a realm somewhat removed from that of discrete energy levels and atomic transitions, though of course it was revealed in the same context of atomic spectra and the effect of applied magnetic fields. This result, which would be "confirmed" in the case of spin in the Stern–Gerlach experiment 5 years later, was based on the quantization rule discovered by Sommerfeld and Wilson[69] (previously mentioned), that the *action* $J = \int p_i \, \mathrm{d}p_i = n_i h$.

It was the speculative leap taken by de Broglie, in proposing that particles ought to possess wave properties, that opened the door for wave mechanics, one of the two early formulations of quantum theory. As we learn from his own words, Schrödinger's most immediate motivation for developing wave mechanics was de Broglie's work,[70] which, along with Einstein's explanation of the photoelectric effect, represented the origin of "wave–particle duality"; Schrödinger was quite explicit about his debt to Einstein.

In passing, the interested reader may want to explore the relationship between Einstein's general relativity and the first tentative gropings toward a quantum mechanics in the early 1920s. It might seem that there could not be much relationship between these two theories, but such is not entirely the case. Hermann Weyl, especially, as an expert in general relativity theory and a mathematical colleague of David Hilbert's, explored these implications of general relativity to the quantum theory.[71] Hilbert himself, whose mathematics, in the hands of John von Neumann and others provided the formal foundation for the quantum theory, very nearly beat Einstein to general relativity.[72]And although little came of these connections, such issues, that is, quantization of gravitation, would be at the forefront of theoretical physics as the 20th century closed.

## CONCLUSION

In 1924, just after de Broglie took his decisive step toward wave–particle duality, Bohr, in a paper with Hendrik Kramers and John Slater, spoke pessimistically of the "doubt . . . whether the detailed interpretation of the interaction between matter and radiation can be given at all in terms of a causal description in space and time of the kind hitherto used for the interpretation of natural phenomena,"[73] signaling that something more than incremental extensions of existing theory would be required.

The state of attempts to explain atomic line spectra and other quantum phenomena was so frustrating to Pauli that in 1924, in the face of what he regarded as ad hoc attempts to play games with integral and half-integral quantum numbers, he declared his intention to give up on it, saying that "I myself have no taste for this sort of theoretical physics and retire from it." This fortunately did not last, and though one could not see it, physics was on the verge of the revolution that would clarify the issues that so troubled Pauli and that would dominate the next decade (and which in some sense is still in progress). Pauli would be one of the most important players. One could say, echoing Abraham Pais in his *Subtle is the Lord* when speaking of the conundrum of the ether, that Pauli's lament was not that "of a single individual, but of an era."[74]

## NOTES

1. See, for example, my *Physics in the Nineteenth Century* (Purrington, 1997). Note that I said "major figures"; there were many others, of course.
2. Who virtually wrote down the Schrödinger equation, as Goldstein (1980) notes.
3. For example, Dugas (1955).
4. Although some oft-quoted statements to that effect cannot be verified.
5. Michelson (1903). In the course of expressing his conviction that " future discoveries must be looked for in the sixth place of decimals," Michelson concluded that "such examination almost surely leads, not to the overthrow of the law."
6. Arguably, perhaps, being repeated by those who think the "theory of everything" is almost at hand.
7. "Nineteenth-Century Clouds Over the Dynamical Theory of Heat and Light," (Kelvin, 1901), delivered in 1900. In a series of very elaborate arguments, he tried to show that the Maxwell–Boltzmann theory of equipartition had to be wrong.
8. There are, of course, problems in classical physics that have only partially succumbed to the vigorous assaults of both mathematicians and physicists, including turbulence and other problems in nonlinear dynamics.
9. The two revolutions, if that is the proper word, clearly also differ in the extent to which quantum mechanics was the offspring of the efforts of at least a dozen important physicists, whereas relativity, although not quite the product of one mind, was nearly so. On precursors such as Poincaré, see Pais (1982).
10. Including Stehle (1994), especially chapters 7–9, Rechenberg (1995), and the chapter *Fin de siecle* in Purrington (1997).

11. Fritz Reiche's *Die Quantentheorie* of 1921 gives an excellent summary of many of these issues. It was translated into English in 1924 by Henry L. Brose, and there was a second edition. In the next chapter, we will consider in greater detail important experimental results from the decade before the new quantum theory came on the scene, about 1915–25. Brose also translated Sommerfeld's work into Engllish.
12. Kuhn (1962).
13. Sommerfeld (1930). See Chapter 5.
14. Actually obtained by John Waterston a decade earlier, in work that was buried for 45 years in the archives of the Royal Society.
15. With $1/2KT$ of energy per degree of freedom (quadratic term in $p$ or $q$ in the energy; that is, $v^2$, $x^2$, $L^2$, etc.). The specific heat at constant volume, $c_v$ is defined as $\partial U/\partial T$ at constant volume, where $U$ is the internal energy. Thus each degree of freedom contributes $1/2k$ to the specific heat., and $c_v = 3/2k$ for a monatomic gas. Alternatively, the molar specific heat is $3/2R$, where $R$ is the universal gas constant (1.99 cal $K^{-1}$ $mole^{-1}$ or 8.3 J $K^{-1}$ $mole^{-1}$). The relationship between $k$ and $R$ is $k = R/N_A$, where $N_A$ is Avogadro's number. See any text on kinetic theory or thermodynamics. Boltzmann's constant $k$ has the value $1.38 \times 10^{-23}$ J/K. It should be noted that tabulated specific heats are usually given in J $K^{-1}$ $g^{-1}$. In the past they were given in terms of calories per gram, and the calorie was defined in terms of the specific heat of water, as the amount of heat required to raise the temperature of 1 g of water 1 °C. Now the calorie is defined in terms of the joule, about 4.2 J. Molar specific heats are more convenient, being, in theory, $nR$, where $n$ is the number of degrees of freedom and $R$=8.3J$K^{-1}$$mole^{-1}$. Admittedly, this is more information than is needed here.
16. Because $c_v = nkT/2$ and $c_p = nkT/2 + kT$; then $\gamma = (n+2)/n$ or $\gamma - 1 = 2/n$.
17. From a BAAS report, quoted in Goldman (1983), p. 118.
18. Maxwell (1875).
19. Rayleigh (1900).
20. The measured $c_v$ makes smooth transitions from $3/2 \rightarrow 5/2$ and $5.2 \rightarrow 7/2$ as increasing fractions of molecules have rotational or vibrational degrees of freedom excited.
21. Thomson's (Kelvin) 1884 Baltimore lectures, as updated and published in 1904, show him pondering this conundrum at great length; it was one of his famous "clouds" that he saw as undermining the classical consensus just before 1900 (Kelvin,1904).
22. Although here the quantum nature of the phenomenon was more obscure, emerging only from its theoretical explanation by Einstein, and later others. The law was formulated in 1819. Petit and Dulong (1819). See Chapter 18. The value $3R$ is about 6 cal$/K$ per mole or about 25 J/K per mole.
23. Einstein (1907).
24. Klein (1965).
25. The $1/\lambda^4$ dependence of the Rayleigh–Jeans law of 1900–1905, which of course blows up at short wavelengths. The term was supposedly coined by Ehrenfest in 1911.
26. Planck (1900). See Kuhn (1978, 1979) or Purrington (1997), pp. 156–7. Planck's introduction of the quantum was vigorously debated at the first Solvay Conference in 1911, where Sommerfeld expressed skepticism that it represented physical reality. See Mehra (1975), p. 39.
27. Before the symbol ħ ("h-bar") was introduced, Dirac employed the symbol $h$ to mean "$h/2\pi$." Planck gave the value of $h$ as $6.55 \times 10^{-27}$ erg-s (Planck, 1900). The accepted value is $6.626\ldots \times 10^{-27}$ erg-s ($6.6 \times 10^{-34}$ J-s).

28. Hertz (1887).
29. Lenard (1902). Lenard was awarded the Nobel Prize in 1905, but became a strong proponent of "Deutsche physic," and an opponent of "jewish physics." Lenard is sometimes confused with the French physicist Alfred-Marie Liénard of the Liénard–Wiechert potential, and perhaps the English physicist John Lennard-Jones, who changed his name from J. E. Jones upon marrying "a Miss Lennard," as Mehra (1972) puts it.
30. Einstein (1905). In no more than two pages.
31. Although Lenard, as a Nazi sympathizer, became an opponent of both relativity and quantum mechanics, he apparently never rejected Einstein's explanation.
32. Einstein (1916b, 1916c, 1917a). The last of these is translated in van der Waerden (1967). Einstein (1916c) essentially established that photons had to carry momentum. These papers were written just as Einstein was revealing general relativity to the world.
33. The controversy that began with the opposing 17th-century views of Robert Hooke and Isaac Newton, up to the consensus achieved in the early 19th-century consensus by Thomas Young that light was a form of wave motion, was an argument about whether light consisted of waves *or* particles, not both.
34. Compton (1923).
35. De Broglie (1924, 1925). Proposed in his PhD thesis of 1924, refereed by Einstein. (See fn. 83 in Rechenberg, 1995.)
36. Davisson, Clinton, and Kunsman (1923), Davisson and Germer (1927a, 1927b; 1928). At Bell Labs after 1925. The entire fascinating story is told in Gehrenbeck (1976). Davisson and G. P. Thomson shared the 1937 Nobel Prize. The story of Thomson's elegant experiments is told in Moon (1977). His results were published in Thomson and Reid (1927), Thomson (1927), etc. It has been "quipped," to quote the AIP website, that J. J. Thomson received the Nobel Prize for showing that the electron was a particle, whereas his son, G. P. Thomson, received it (1937) for showing that it wasn't. Germer did not share the prize in 1937, which was awarded to Davisson and Thomson.
37. Bailey and Townsend (1921), and succeeding papers; Ramsauer (1921).
38. Elsasser (1925).
39. This would be Davisson and Kunsman (1923); Davisson and Germer, (1927a). See Jammer (1966, p. 249) for elaboration, including the contributions of Elsasser. See also the AIP Oral History interview with Elsasser, Nov. 21, 1985.
40. Characteristic x-ray spectra represented a similar issue, but this was discovered only in 1913.
41. Ritz (1908a). It stated that spectral line frequencies were either the sum or difference of another pair of lines. This was a first step toward the understanding that spectral lines represent the difference between the energies of two atomic levels.
42. Franck and Hertz (1914). Translated in Ter Haar (1967).
43. Bohr (1915b). That the results of the Franck–Hertz experiment were obtained in April 1914, not long after Bohr's first paper on hydrogen.
44. Röntgen (1895). A translation by Arthur Stanton appeared in *Nature* the next year (Röntgen, 1896). The discovery, made in Würzburg on Nov. 8, 1895, led to his being awarded the first Nobel Prize, in 1901. Element 111, Roentgenium, is named after him.
45. Moseley (1913, 1914). He obtained expressions for the frequency of these lines whose $Z$-dependence was modified by screening. . Moseley perished at the battle of Gallipoli on Aug.10, 1915, age 27, along with about 130,000 others.

46. Becquerel (1896).
47. Just over a century ago. His major assistants and collaborators were Soddy, Geiger, Marsden, and later Chadwick.
48. The "discovery," or identification, of the electron in 1897 by J. J. Thomson (Thomson 1897a,1897b) as the quantum of electrical charge, itself had implications not very different from those we have been discussing.
49. Again, Stehle (1994) provides an accessible summary of these developments.
50. Independently by Gurney and Condon. See Chapter 15.
51. As is well known, the 1921 Nobel Prize was awarded to Einstein for his explanation of the photoelectric effect (but was delayed until 1922), but not really for the notion of a quantum of electromagnetic energy. It would have been awarded for special relativity, but this had become conflated with general relativity, about which there was much skepticism. Nonethless, Einstein devoted his Nobel Lecture to relativity. It is also well known that Einstein ultimately rejected the offspring of his idea of the quantum of energy, standard or orthodox quantum theory. When confronted by Phillip Frank about this, with Frank saying that the viewpoint of Heisenberg and Bohr "was invented by you," Einstein supposedly replied that "a good joke should not be repeated too often." See Frank's notes on Einstein [Frank (1947), p. 216; quoted in Jammer (1974), p. 131]. Rosenfeld (1971) has pointed out that for some time an alternative explanation of the Compton effect in terms of the Doppler effect was possible.
52. Jammer (1974), p. 126. An obvious choice once "electron" had been coined by Stoney in 1894 for the quantum of electric charge.
53. See Mehra (1975) for details. The subject was "The Theory of Radiation and the Quanta." Sommerfeld and Rutherford were among the 20+ attendees as well, but not Bohr, who was just completing his PhD dissertation. The second Solvay Conference took place just weeks after Bohr's paper was published, and he was again not an attendee, and the third Solvay Conference was not held until after the war, in 1921.
54. Poincaré (1912).
55. See McCormmach (1967).
56. Condon and Morse (1929). ter Haar, (1967).
57. *Vorlesungen über Atommechanik*, 1925; quoted in Condon and Morse (1929), pp.7–8.
58. Bohr (1913a). "On the consititution of atoms *and molecules*." These are reproduced, in part, in French and Kennedy (1985). The initial paper is also reprinted in ter Haar (1967). For a secondary work, see Heilbron and Kuhn (1969).
59. It is interesting to see Bohr correctly concluding that there were closed shells involving 2, 8, and 18 electrons, well before the Pauli principle. But he had no real theory, and his 18 electrons were divided into three groups of six, rather than 2 + 8 + 10. Bohr (1921). See also Chapter 10.
60. The three centers of activity were Munich, under Sommerfeld, Göttingen, under Born, and Copenhagen, under Bohr.
61. On the technical meaning of "action" and the "principle of least action" in mechanics, see, for example, Goldstein (1980).
62. For example, Merzbacher (1998), p. 2.
63. Condon and Morse (1929), p. 8.
64. Bohr (1925). The paper is an excellent introduction to the situation in late 1925, shortly after Heisenberg's paper appeared and just before Born and Jordan (1925). It includes a

discussion of the “quantization rule.” In some respects Bohr was the most conservative of the founders of the quantum theory, holding onto classical concepts to the last—around 1920. When he died in 1962 things were very different. See Hendry (1984), pp. 28–34.

65. It officially became the Neils Bohr Institute in 1965. Lorentz, who was still a towering figure, died in early 1928, age 75.
66. “Fundamental Postulates,” Bohr (1922). See Hendry (1984), p.141
67. “On the quantum theory of line spectra,” published in three parts between 1918 and 1922. See van der Waerden (1967), pp. 5–8. Van der Waerden printed only part I. The three papers are collected in the reprint volume, Bohr (2005). Bohr first used the term “correspondence principle” [*Korrespondenzprinzip*] in 1920 (Bohr, 1920). *Zeitschrift fur Physik* had just began publishing that year.
68. Sommerfeld (1916b). Debye (1916), the article succeeding Sommerfeld’s.
69. Sommerfeld (1916b). See ter Haar (1967), p. 75; Wilson (1915). In this case, William Wilson.
70. De Broglie (1924). De Broglie received the 1929 Nobel Prize in Physics.
71. Rather than cite papers by Weyl in this case, I refer the reader to chapter 2 of Hendry’s book (1984).
72. The subject of much controversy.
73. Bohr, Kramers, and Slater (1924).
74. Pais (1982), p. 115.

# 2

## 1913: THE BOHR THEORY OF THE HYDROGEN ATOM

Quantum *theory* was born in the first decade of the 20th century with the papers of Planck and Einstein.[1] But quantum *mechanics,* as a dynamical theory of the microscopic world, had its beginning in Niels Bohr's seminal paper in *Philosophical Magazine* in 1913,[2] showing how certain assumptions about the role of quanta could explain the Balmer series discrete spectrum of the hydrogen atom. This paper holds a deservedly honored place in the history of quantum mechanics, at least rivaling those of Heisenberg and Schrödinger a little over a decade later, and everything that took place between 1913 and 1927 built upon Bohr's theory.

The essential building block was Rutherford's hypothesis of 1911, based on his experiments with $\alpha$-particles,[3] that the atom consisted of a small, massive central core and a surrounding electron cloud. After a couple of meetings with Rutherford, one in Manchester and the other at Cambridge, Bohr was invited to work in his laboratory in Manchester (see Figure 2.1). He spent less than 5 months with Rutherford, but there he became quite familiar with the latter's nuclear atom.[4] But he knew that the orbit of an electron circling a positively charged central body would be unstable because an accelerated charged particle must radiate electromagnetic energy according to Maxwell's electromagnetism. To explain the stability of the hydrogen atom, that is, the existence of "stationary states," and lacking any real theory other than classical mechanics and the notion of the quantum, Bohr simply *postulated* that an electron would be in a stable orbit if it satisfied certain integral or quantum conditions.[5] This was, of course, an ad hoc explanation—or, if you prefer, merely a recognition of an empirical fact that would require over a decade to find an explanation for. In part because of Bohr's chronic prolixity, or one might say, his penchant for thinking out loud in print, a reader might be excused for not seeing how what is taught as the "Bohr theory" emerged from his papers of 1913–1915. But it cannot be emphasized too strongly that it was Bohr's fundamental insight that spectral lines resulted from transitions *between* discreet stationary states; that is, a line did not itself correspond to a state. This, coupled with the assumption finally reached by Bohr that the energy difference given up in a transition between two states was radiated as a *single* photon, an argument that evolved in these papers, provided the basis for Bohr's theory of the atom. Of course, Bohr does not speak of photons, because the name would not appear for over a decade. Rather he uses the term "energy quanta," but there is more to the story. In fact, as late as 1920 (and beyond) Bohr was unable to accept the idea

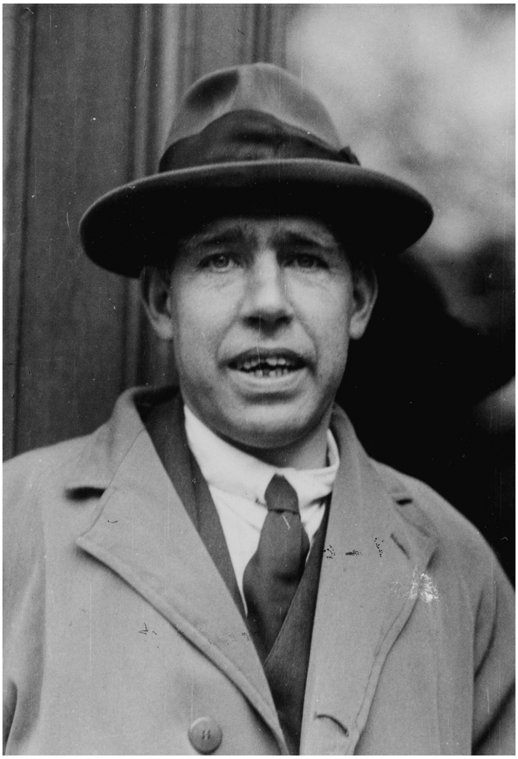

**Figure 2.1.** Niels Bohr (1885–1962). AIP Emilio Segrè Visual Archives, Segrè Collection.

of the photon. I recommend especially Pais's discussion of the issue in his *Niels Bohr's Times*.[6] Bohr's quantum postulate was that instead of radiating energy continuously as required by Maxwell's theory, the energy was emitted as electromagnetic quanta with energy $h\nu$,[7] and only when an electron changed orbits. This insight, for which Bohr credits Einstein's papers of 1905–1907, would lead to a quantization condition for the stable orbits themselves.[8]

But the road to the correct result was, and still is, a bumpy one. Bohr's starting point was the *assumption* that when an electron falls in from *infinity* to a stable orbit with orbital frequency $\omega$, radiation with a frequency $\nu = \omega/2$ would be emitted,[9] and that the energy emitted, $W$, "from Planck's theory," would be an integral multiple of $h\nu$. That is, $W = nh\nu = nh\omega/2$, which would be the negative of the energy of the bound electron. This is the quantum condition, of which Leon Rosenfeld has written that "the daring (not to say scandalous) character of Bohr's quantum postulate cannot be stressed too strongly."[10] And in December of 1913, shortly after the final part of the trilogy appeared, Sir James Jeans complained that "The justification of his theoretical assumptions is only the very ponderous one of success."[11] Bohr's reasoning apparently was that if the orbital frequency at infinity is 0, and for the final orbit, $\omega$, then the emitted radiation could be assumed to have frequency $\nu = \omega/2$. Not a very sound argument but one that led to the correct result, which was certainly a strong motivation for him.

Now it is easy to show, classically, that for a circular orbit, $\omega$ is proportional to $E^{3/2}$ (Kepler's Third Law; Bohr's Eq. 1), specifically,[12]

$$\omega = \left(2^{1/2}/m^{1/2}k\pi\right)W^{3/2}, \tag{2.1}$$

where $E$ is the energy of the electron. The result is that the energy radiated by an electron falling in from infinity would be proportional to $\omega^{2/3}$. But Bohr had to introduce the quantum postulate, essentially $E = nh\nu$ and his leap of faith, or guess, was to take $\nu = \omega/2$. Then, using the assumption that $W = -E = nh\omega/2$ to eliminate $\omega$, one finds that (Bohr's Eq. 3)

$$E = -2\pi^2 mk^2/\left(n^2h^2\right), \tag{2.2}$$

in which the Coulomb potential energy has been written[13] as $V = -k/r$. This appears to give the correct expression for the energies of the stationary states in hydrogen, except that the orbits are labeled by the number of quanta, $n$, emitted as the electron falls in from infinity. But Bohr noted that $W$ is greatest when $n = 1$ corresponding to the ground state, and that this leads to $W = 13$ eV, the correct binding energy of an electron in the ground state, essentially the Rydberg constant. But this requires that a *single* quantum of energy be emitted in the transition to the ground state, which is what Bohr would eventually adopt, in his sec. 3. This is fine, but what are we to make of the states labeled by different values of $n$?

The way to look at this is to say that Bohr had an expressions for $E(\nu)$, the quantum one, and a classical expression for $E(\omega)$, both of which he took to be valid. This required a relation between $\nu$ and $\omega$ that he took to be $\nu = \omega/2$ a leap of faith with the dubious justification previously given. Then, eliminating $\omega$ led to Eq. (2.1) with $W$ or $E$ proportional to $1/n^2$.

In his sec. 2, we see Bohr beginning to sour on his original assumptions, for as he continued on with the Balmer series, in which the energy emitted in a transition from level $n_2$ to $n_1$ would be of the form $E_{2\to1} = 2\pi^2 mk^2\left(1/n_1^2 - 1/n_2^2\right)$, with $n_2 = 2$ and $n_1 > 2$, to get the correct expression for the frequencies, he now had to accept that the energy was emitted in the form of *a single* quantum, that is, $E_{2\to1} = h\nu$ abandoning, as was said, his original postulate. From this, however, followed the basic features of the emission or absorption spectra of hydrogen, and the Balmer formula, involving a transition from $n = 3, 4, 5, \ldots$ to $n = 2$, follows immediately. While doing all this, however, Bohr deferred a discussion of the validity of his assumptions until later in the paper. The result stood but the reasoning had to be revised. The meaning of the quantum number $n$ had been reinterpreted, with considerable sleight of hand. Rarely has such an important proof rested on such flimsy foundations, something Bohr evidently recognized.

Then, in his sec. 3, Bohr says that "we will now return to the discussion of the special assumptions used in deducing the expressions . . . for the stationary states of the system. . . ." and describes the assumption that different numbers of quanta are emitted during transitions as "improbable." After a bit of effort, he concludes that "we are thus led to assume that the interpretation . . . is not that the stationary states correspond to the emission of different numbers of energy-quanta, but that the energy emitted . . . is equal to different multiples of $\omega/2$." So rather than $n$ quanta with frequency $\nu$, only a single quantum is emitted, with energy $h\nu$ but $\nu = n\omega/2$. Why a *single* quantum? Again, the justification is that it worked. Bohr relaxed his original assumption but still assumed that $W$ is still linearly related to $\omega$: $W = f(n)h\omega$ and showed, using the correspondence principle, that $f(n) = n/2$. Of course it gives precisely the same result, but, as we have said, the meaning of n has changed. Unlike most scientific papers, which give only the finished product, the final reasoning, this one allows us to see how Bohr's thinking evolved as he struggled to justify what was obviously the correct formula, with little to guide him. The result was pretty much a muddle.

On the other hand, it is also easy to show from classical mechanics that for any level with energy $E$, the energy can be expressed as:

$$E = -mk^2/\left(2L^2\right), \tag{2.3}$$

where $L$ is the orbital angular momentum, whence, by combining Eqs. (2.2) and (2.3), we have $L = nh/2\pi = n\hbar$, which is the quantization condition for angular momentum. Although Bohr makes note of this almost as an afterthought, and dismisses it with the statement that "there obviously can be no question of a mechanical foundation of the calculations given in this paper . . . ," the "Bohr postulate" is often taken to be just that: quantization of the orbital angular momentum. Despite the historical inaccuracy, we can then argue, ignoring the initial "proof," that the Bohr theory rests on this *postulate*, $L = nh$. Another writer, having discovered that the angular momentum was quantized, might have used that as his postulate and suppressed the earlier arguments, but not Bohr. And, in fact, in sec. 5 of the paper, and in the second installment, Bohr notes that in "the permanent state" of an atom, that is, the ground state, the angular momentum of an electron[14] is $h/2\pi$, and really doesn't look back.

A decade after Bohr's original papers, following de Broglie, it could be shown that this quantum condition $L = nh$ was equivalent to the postulate that an integral number of de Broglie wavelengths ($\lambda = h/p$) would fit into one orbit.[15] Interestingly, had he been able to use the later Wilson–Sommerfeld quantization rule,[16] which would have said that $\int p\,\mathrm{d}q = nh = \int L\,\mathrm{d}\theta = 2\pi L$, he would have immediately found that $L = nh/2\pi = nh$.

Beyond the fundamental result of the paper, Bohr concluded more generally that bound or closed systems will possess discrete, stationary states, but that unbound systems will still have continuous spectra. The successful application of Bohr's theory to the experiments of E.C. Pickering and William Fowler on ionized helium was another great triumph,[17] but it was soon apparent that even two-electron atoms posed insurmountable problems. In the last two parts of the trilogy, Bohr attacked the problems of multielectron atoms and even molecules, without notable success. In part III, he attempted to explain the stability of multinuclear molecules by invoking the principle of "universal constancy of the angular momentum of the bound electrons."[18]

It is worth noting that the 27-year-old Bohr was not working in a vacuum.[19] He was strongly influenced by John William Nicholson, whose atomic models owed more to J. J. Thomson than to Rutherford, but did include quantization of angular momentum to attain stability.[20] Nicholson was thus the first to attempt a quantum-mechanical theory of the atom. And although Bohr's triumph (along with Rutherford's discoveries), provided the impetus for all that followed, the elation was short-lived, as attempts to extend his approach, by Bohr himself and by Sommerfeld and others, met with failure almost from the outset. The result was a decade of floundering attempts to find a theoretical description of the mass of spectroscopic data that was accumulating that bore little fruit.

## CONCLUSION

Bohr's theory was embraced almost immediately, despite its logical shortcomings. It is likely that readers of his paper were able to look beyond these original shaky foundations and accept quantization of orbital angular momentum as a fundamental principle. Einstein, for example, quickly saw its importance, and in 1916 called it "a miracle," and "the highest musicality in the sphere of thought."[21] Many, like Moseley, took several months to be persuaded, and some, like Johannes Stark, were unconvinced a decade later. J. J. Thomson complained that the theory was only mathematical, not dynamical,[22] and some resistance was based, quite reasonably, on the fact that the theory was capable of explaining the structure of only a single element. Runge thought it was "the sheerest nonsense," and Paul Ehrenfest called it "completely monstrous." [23] Constraints of space will not allow a recount of the fascinating story of the reception of the Bohr theory, but it has been described in several places.[24] As we saw in the last chapter, the famous Franck–Hertz experiment of the year after the Bohr theory, in which electrons were found to be absorbed by mercury atoms only if their energies were 4.9 eV (to use modern terminology), provided strong support for the idea of discrete electronic states as in Bohr's theory.

In a sense that goes far beyond the Bohr theory of hydrogen or the failed Bohr–Sommerfeld theory, Neils Bohr was the father of quantum theory, even quantum theory as we understand it today. Bohr thought more deeply and more continuously than anyone else about the fundamental questions that led, almost inexorably, to the discoveries of the late 1920s, often aided by his correspondence principle, which, though much neglected today, was the guiding light for a generation of young quantum physicists.[25] All of the founders of quantum mechanics visited Bohr in Copenhagen at one time or another, and the long walks with Bohr, the arguments and discussions, gave impetus to the discoveries that would follow. Without Bohr's influence, it is doubtful that the revolution would have come when it did.[26]

While we have dwelt rather heavily on the deficiencies in Bohr's arguments, we have also noted that most authors would have suppressed the reasoning that Bohr himself found faulty and would have published a cleaned-up version. Bohr was not awarded the Nobel Prize in physics until 1922, simultaneously with Einstein, who was belatedly awarded it for the year 1921, but the delay was as much the result of the war as of misgivings about the theory.[27]

## NOTES

1. Planck (1900, 1901), Einstein (1905, 1907).
2. Actually a 71-page trilogy; Bohr (1913a). The three parts were published in July, September, and November. An excellent source is Heilbron and Kuhn (1969). See also Heilbron (1985) and Stachel (2009).
3. See Chapter 15.
4. See Rudolf Peierls's Rutherford Lecture, delivered in November 1987 (Peierls, 1997). He died in 1995. It has been said that Rutherford took to Bohr because he was a "footballer," depite their very different personalities and approach to physics.
5. The interested reader might consult the paper by Pais (1995), in which the contributions of Haas, Nicholson, and Bjerrum are detailed. On antecedents, see especially pp. 80–82.
6. Pais (1991).
7. Note that this is not equivalent to adopting the photon picture of light, which Bohr did not quickly do.
8. This is the birth of the idea of a quantum state. See Weisskopf (1985, in French) and Kennedy (1985).
9. Almost the only plausible basis for this assumption would appear to be simply that it leads to the correct expression for the hydrogen spectra, with the correct Rydberg constant. For background, see the detailed discussion in Heilbron (1985), pp. 45–6. Bohr was using an analogy with a Planck oscillator, which he eventually abandoned. Note that in Bohr, $\omega$ is frequency ($s^{-1}$), not angular frequency. The first part of the paper, beginning on p. 1 of vol. 26 of the *Philosophical Magazine* (Bohr, 1913a), is reproduced, with slight modification, in Ter Haar (1967). Unfortunately Bohr's endnotes are omitted.
10. Referring in part to the next assumption as well. Heilbron (1985), more gently, called it an invention and the derivation "unintelligible." The interpretation given here, however, is my own. The flaws in the proof don't stop there, as we shall see. In fairness to Bohr, however, one should note his caveat, "the question, however, of the rigorous validity of both assumptions . . . will be more closely discussed in § 3."
11. Quoted in Hund (1974), p. 74.
12. Bohr used $W$ for the orbital energy; I am using both $W$ and the conventional symbol $E$.
13. Bohr wrote it as $Ee/r$, and we would write $Ze/r$. He also used $\tau$ for the integral number of quanta rather than $n$.
14. Actually for" every electron" in a multielectron atom (Bohr, 1913a, part II, p. 477) Obviously the exclusion principle was over a decade away.
15. For a circular orbit the circumference $C$ equals $2\pi r$, but with $L = n\hbar = mvr$, it follows that $C = 2\pi L/mv = 2\pi L/p$. With $p = h/\lambda$ from the de Broglie formula, $C = n\lambda$, de Broglie shows this more generally (de Broglie, 1924).
16. Wilson (1915), Sommerfeld (1916c). Sometimes called Bohr–Wilson–Sommerfeld.
17. Pickering (1896), Fowler (1912). Ionized helium, of course, is the same problem as hydrogen, with a larger nuclear mass and charge.
18. The quote is actually from part II, p. 502, but invoked as well in part III.
19. See Heilbron (1977), p. 40.

20. Nicholson (1911, 1912). See McCormmach (1966). Also an unpublished online paper by Jaume Navarro, "The structure of the atom before Bohr." See, as well, Nagaoka's "saturnian" model.
21. Quoted in Kragh (2010a).
22. Thomson (1919), p. 420.
23. Footnotes 9 and 154 in Kragh (2010). The entire paper is of interest.
24. For the period 1913–1915, see Kragh (2010a), and references therein.
25. Bohr (1920). English translation in *Neils Bohr, Collected Works* (1976), p. 241. Dirac once said that Bohr "seemed to be the deepest thinker that I ever met." Quoted in Kragh (1990), p. 38. John Slater felt quite differently, particularly regarding the apparent absence of mathematical underpinnings for his work. See the AHQP Oral History interview.
26. Unfortunately, Bohr died suddenly in 1962 before extensive interviews by historians of science could plumb the depths of his memory.
27. Kragh (2010).

# 3

## TYRANNY OF THE DATA
## ATOMIC SPECTROSCOPY TO 1925

### INTRODUCTION

In the first chapter we surveyed a series of important empirical results from the period straddling the turn of the century that seemed to defy explanation in terms of accepted classical physics. Some of these phenomena, like blackbody radiation, the photoelectric effect, and (later) Compton scattering, required, or at least were a motivation for, the introduction of the quantum of electromagnetic energy, the photon.[1] Others, such as the problem of specific heats of gases, would eventually demand the quantization of internal degrees of freedom of a system. It was, however, in the problem of atomic line spectra and characteristic x-ray spectra that experiments most clearly established the need for a radical theoretical transformation. By 1920 an enormous mass of spectroscopic data awaited some kind of theoretical interpretation,[2] and because these empirical results were so crucial in forming the basis for the theoretical developments that are our main preoccupation, some time is now devoted to the recounting of these discoveries.[3]

Before embarking on this discussion of atomic spectra, however, we should note that although the scattering experiments of Rutherford and his colleagues established the reality of the nuclear atom in 1909–1911,[4] it had taken some time to arrive at the number of electrons per atom; hence the equality of the atomic number and the number of electrons (or about one electron per two units of atomic weight).[5] J. J. Thomson and Charles G. Barkla[6] played perhaps the most important roles in working this out by about 1911. In the Thomson or even Nicholson models of the atom, the charge was distributed uniformly, and the disparity between the mass of the atom and tiny electron mass meant that the number of charges had to be huge. But if the charge on the atom was approximately equal to the atomic number, there must be a large amount of "positive electrification" as well. Sommerfeld's classic and enormously influential *Atomic Spectra and Spectral Lines* [*Atombau und Spektrallinien*] noted that Phillipp Lenard had attempted to understand x-ray scattering from the atom by arguing in 1903 that matter had a "perforated structure," with only a "tiny part impenetrable to x-rays."[7] But by 1920, with the Bohr–Rutherford nuclear atom well established, James Chadwick was able to show that the observed deflections in Coulomb scattering from various nuclei confirmed the fact that the nuclear charge was the same as the atomic number.[8] We discuss this further in Chapter 15.